Table 2-5.1 Emission Factors, Aldehydes and Ketones, (continued)

	Arapahoe		TIDD Plant	Air Pol (Shawnee)		
	Baseline	SNCR		GSA+ESP	GSA+FF	GSA+ESP+FF
Units: lb/10^{12} Btu						
Acetone			ND< 3.3 N			
Acetaldhyde						
Acrolein						
Benzaldehyde						
2,5-Dimethyl benzaldehyde						
n-Butyraldehyde						
2-Butanone (Methyl ethyl ketone)			ND< 3.3 N			
Crotonaldehyde						
Formaldehyde	17 U		5.1			
Hexaldehyde						
2-Hexanone			ND< 3.3 N			
4-Methyl-2-Pentanone			ND< 3.3 N			
Propanal (Propionaldehyde)						
o-Tolualdehyde						
m/p-Tolualdehyde						
Valeraldehyde						
iso-Valeraldehyde						
1,4-Benzoquinone						

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confidence Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.2 Emission Factors, Dioxins

Units: lb/10^{12} Btu	Coal Creek	Boswell	Springerville	Cardinal	
				Non Soot Blowing	Soot Blowing (Only One Sample Taken)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	ND< 2.0e-06 #	8.1e-07 AU		ND< 1.6e-06 #	ND< 4.3e-07 #
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	ND< 2.4e-06 #	ND< 1.4e-06 A		ND< 1.7e-06 #	ND< 2.0e-06 #
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	ND< 2.1e-06 #	ND< 2.8e-06 BU		ND< 1.9e-06 #	6.0e-07 N
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	ND< 3.2e-06 #	ND< 1.4e-06 A		ND< 1.3e-06 #	ND< 2.7e-06 #
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	ND< 3.3e-06 #	ND< 1.4e-06 B		ND< 1.1e-06 #	ND< 2.7e-06 #
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	3.2e-06 U	ND< 1.4e-06 B		2.3e-06 AN	2.3e-06 N
Octachlorodibenzo-p-dioxin	1.5e-05 U	ND< 1.1e-05 BU		2.0e-05 N	1.9e-05 N
Total Tetrachlorodibenzo-p-dioxin		9.3e-06		ND< 5.23-05 AN	1.7e-06 N
Total Pentachlorodibenzo-p-dioxin		4.6e-06		ND< 3.0e-05 #	ND< 2.3e-05 #
Total Hexachlorodibenzo-p-dioxin		2.1e-06 U		ND< 2.2e-05 BN	6.0e-07 N
Total Heptachlorodibenzo-p-dioxin		ND< 1.9e-06 #		ND< 7.6e-06 AN	2.3e-06 N
Total PCDO		2.03-05			
Total Dioxins and Furans			ND< 6e-06 #		

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confidence Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.2 Emission Factors, Dioxins, (continued)

	Baldwin	Niles	SNOX	Yates	Bailly
Units: lb/10^{12} Btu					
2,3,7,8-Tetrachlorodibenzo-p-dioxin	ND< 2.5e-06 BU	ND< 2.1e-06 #			
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	ND< 4.2e-07 #	ND< 2.9e-06 #			
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	ND< 4.2e-07 #	ND< 3.4e-06 #			
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	ND< 3.2e-07 #	3.0e-06 BU			
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	ND< 4.2e-07 #	2.9e-06 BU			
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	ND< 1.3e-06 A	1.7e-05 U			
Octachlorodibenzo-p-dioxin	ND< 8.9e-06 AU	1.9e-05 U			
Total Tetrachlorodibenzo-p-dioxin	1.3e-06				
Total Pentachlorodibenzo-p-dioxin	ND< 7.4e-07 B				
Total Hexachlorodibenzo-p-dioxin	9.6e-07 U				
Total Heptachlorodibenzo-p-dioxin	2.5e-06 AU				
Total PCDD	1.1e-05 U				
Total Dioxins and Furans					

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confidence Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.2 Emission Factors, Dioxins, (continued)

	Nelson Dewey	Hammond	Smith	Burger	
Units: lb/10^{12} Btu				Baseline	SNRB
2,3,7,8-Tetrachlorodibenzo-p-dioxin				3.4e-06 BU	ND< 1.9e-06 BN
1,2,3,7,8-Pentachlorodibenzo-p-dioxin				ND< 3.3e-06 #	1.7e-05 BU
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin				ND< 3.3e-06 #	4.1e-05 BU
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin				ND< 3.3e-06 #	4.4e-05 BU
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin				ND< 4.1e-06 BN	8.9e-05 AU
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin				9.4e-06	5.2e-04 AU
Octachlorodibenzo-p-dioxin				2.6e-05 U	1.4e-03 U
Total Tetrachlorodibenzo-p-dioxin				3.4e-06 BU	1.0e-05 BU
Total Pentachlorodibenzo-p-dioxin				ND< 3.3e-06 BN	6.3e-05 BU
Total Hexachlorodibenzo-p-dioxin				2.8e-06 BU	3.2e-04 AU
Total Heptachlorodibenzo-p-dioxin				1.6e-05	9.2e-04 AU
Total PCDD					
Total Dioxins and Furans					

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confidence Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.2 Emission Factors, Dioxins, (continued)

	Arapahoe	TIDD Plant	AirPol GSA (Shawnee)
Units: lb/10^{12} Btu			
2,3,7,8-Tetrachlorodibenzo-p-dioxin		ND< 2.0e-06 -N	
1,2,3,7,8-Pentachlorodibenzo-p-dioxin		ND< 3.5e-06 -N	
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin		ND< 4.8e-06 #	
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin		ND< 3.9e-06 -N	
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin		ND< 4.4e-06 -N	
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin		7.3e-06	
Octachlorodibenzo-p-dioxin		7.7e-05	
Total Tetrachlorodibenzo-p-dioxin		ND< 1.8e-06 AN	
Total Pentachlorodibenzo-p-dioxin		ND< 3.5e-06 N	
Total Hexachlorodibenzo-p-dioxin		ND< 4.1e-06 N	
Total Heptachlorodibenzo-p-dioxin		1.4e-05	
Total PCDD			
Total Dioxins and Furans			

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confidence Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.3 Emission Factors, Furans

	Coal Creek	Boswell	Springerville	Cardinal		Baldwin
Units: lb/10^{12} Btu				Non Soot Blowing	Soot Blowing (Only One Sample Taken)	Non Soot Blowing
2,3,7,8-Tetrachlorodibenzofuran	9.9e-06	6.0e-06		6.6e-07 BU	ND< 1.8e-06 #	ND< 1.3e-06 AU
1,2,3,7,8-Pentachlorodibenzofuran	ND< 4.3e-06 #	5.6e-06		ND< 1.0e-06 #	ND< 2.3e-06 #	ND< 7.4e-07 A
2,3,4,7,8-Pentachlorodibenzofuran	ND< 3.7e-06 #	5.1e-06		ND< 1.3e-06 #	ND< 3.1e-06 #	1.8e-06
1,2,3,4,7,8-Hexachlorodibenzofuran	ND< 3.8e-06 #	6.5e-06		ND< 1.7e-06 #	ND< 2.5e-06 #	2.4e-06
1,2,3,6,7,8-Hexachlorodibenzofuran	ND< 3.1e-06 #	2.2e-06		ND< 1.3e-06 #	8.4e-07 N	8.0e-07
1,2,3,7,8,9-Hexachlorodibenzofuran	ND< 5.3e-06 #	ND< 1.4e-06 B		ND< 1.4e-06 #	ND< 2.3e-06 #	ND< 3.2e-07 #
2,3,4,6,7,8-Hexachlorodibenzofuran	ND< 1.9e-06 #	2.3e-06		ND< 1.9e-06 BN	ND< 2.9e-06 #	ND< 1.5e-06 B
1,2,3,4,6,7,8-Heptachlorodibenzofuran	ND< 2.3e-05 #	4.6e-06		2.0e-06 AU	ND< 2.3e-06 #	1.5e-06
1,2,3,4,7,8,9-Heptachlorodibenzofuran	ND< 3.8e-06 #	ND< 2.8e-06 A		ND< 1.9e-06 #	ND< 2.5e-06 #	ND< 4.6e-07 #
Octachlorodibenzofuran	6.3e-06 A	1.9e-06 U		1.1e-05 U	7.8e-06 N	4.2e-06 U
Total Tetrachlorodibenzofuran		6.0e-05		ND< 3.5e-05 AN	ND< 7.0e-05 #	ND< 3.8e-06 B
Total Pentachlorodibenzofuran		4.7e-05 U		2.8e-06 U	ND< 7.6e-05 #	4.0e-06
Total Hexachlorodibenzofuran		2.2e-05		ND< 2.5e-05 AN	3.9e-06 N	5.6e-06 U
Total Heptachlorodibenzofuran		7.0e-06		2.7e-06 AU	ND< 9.8e-06 #	3.2e-06
Total PCDF		1.4e-04				1.8e-05
Total Dioxins and Furans			ND< 6e-06 #			

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.3 Emission Factors, Furans, (continued)

	Niles	SNOX	Yates	Bailly	Nelson Dewey	Hammond
Units: lb/10^{12} Btu						
2,3,7,8-Tetrachlorodibenzofuran	4.8e-06 BU					
1,2,3,7,8-Pentachlorodibenzofuran	ND< 3.4e-06 #					
2,3,4,7,8-Pentachlorodibenzofuran	3.2e-06 BU					
1,2,3,4,7,8-Hexachlorodibenzofuran	9.6e-06 BU					
1,2,3,6,7,8-Hexachlorodibenzofuran	3.8e-06 BU					
1,2,3,7,8,9-Hexachlorodibenzofuran	6.5e-06 AU					
2,3,4,6,7,8-Hexachlorodibenzofuran	ND< 2.5e-06 #					
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.7e-05 AU					
1,2,3,4,7,8,9-Heptachlorodibenzofuran	3.6e-06 BU					
Octachlorodibenzofuran	2.0e-05 U					
Total Tetrachlorodibenzofuran						
Total Pentachlorodibenzofuran						
Total Hexachlorodibenzofuran						
Total Heptachlorodibenzofuran						
Total PCDF						
Total Dioxins and Furans						

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.3 Emission Factors, Furans, (continued)

	Smith	Burger		Arapahoe	TIDD	AirPol (Shawnee)
Units: lb/10^{12} Btu		Baseline	SNRB			
2,3,7,8-Tetrachlorodibenzofuran		ND< 2.5e-06 AN	4.1e-05 U		ND< 2.0e-06 BN	
1,2,3,7,8-Pentachlorodibenzofuran		ND< 3.3e-06 #	3.3e-05 BU		ND< 2.2e-06 BN	
2,3,4,7,8-Pentachlorodibenzofuran		ND< 4.9e-06 #	6.1e-05 U		ND< 2.2e-06 BN	
1,2,3,4,7,8-Hexachlorodibenzofuran		ND< 4.9e-06 #	3.4e-06 N		5.6e-06	
1,2,3,6,7,8-Hexachlorodibenzofuran		1.2e-06 N	1.1e-06 AN		ND< 2.2e-06 BN	
1,2,3,7,8,9-Hexachlorodibenzofuran		3.7e-06	2.2e-04 U		ND< 3.5e-06 -N	
2,3,4,6,7,8-Hexachlorodibenzofuran		ND< 2.5e-06 #	1.4e-05 BU		4.4e-06	
1,2,3,4,6,7,8-Heptachlorodibenzofuran		ND< 1.1e-04 #	1.2e-03 BU		6.4e-06 A	
1,2,3,4,7,8,9-Heptachlorodibenzofuran		ND< 8.2e-06 AN	1.6e-04 AU		ND< 5.0e-06 #	
Octachlorodibenzofuran		2.1e-05	7.0e-04 U		1.2e-05 A	
Total Tetrachlorodibenzofuran		6.8e-06 U	9.0e-05 U		ND< 2.0e-06 BN	
Total Pentachlorodibenzofuran		ND< 3.3e-06 BN	2.8e-04 U		4.3e-06 A	
Total Hexachlorodibenzofuran		1.6e-05 U	2.3e-03 U		1.4e-05	
Total Heptachlorodibenzofuran		9.0e-06	1.6e-03 AU		4.5e-06 A	
Total PCDF						
Total Dioxins and Furans						

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC)

	Coal Creek	Boswell	Springerville	Cardinal	Baldwin	Niles	SNOX
Units: lb/10^{12} Btu				Non Soot			
Carbon Disulfide	3.4 B	18 U		ND< 51 AN	0.14 AU	5.9 AU	5.4 B
Bromomethane (Methyl Bromide)	4.3 AU			15 AU	0.97 BU	ND< 6.5 #	9.6 A
1,2-Dibromomethane				ND< 2.0 #			
Bromodichloromethane	ND< 6.5 #			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
Dibromochloromethane	ND< 6.5 #			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
Dibromoethane (Ethylene Dibromide)		0.066 BU					
Tribromomethane (Bromoform)	3.1 B			ND< 10 #		ND< 4.9 #	ND< 5.8 #
Chloromethane	106	2.5		6.4 AU		4.9 BU	218 U
Dichloromethane (Methylene Chloride)	NC	11		ND< 13 N	18		
Trichlorofluoromethane		1.8 U		15	2.6		
Trichloromethane (Chloroform)	ND< 6.5 #			2.9 A		ND< 5.1 #	ND< 5.8 #
Carbon Tetrachloride	ND< 6.5 #			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
Iodomethane				9.6 B	0.43 BU		
Bromoethene				ND< 12 #			
Chloroethane (Ethyl Chloride)	ND< 6.5 #	2.5 AU		ND< 10 #		ND< 5.1 #	3.4 B
1,1-Dichloroethane (Ethylidene Dichloride)	ND< 6.5 #			ND< 1.8 #		ND< 5.1 #	ND< 5.8 #
1,2-Dichloroethane	3.2 B			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
1,1,1-Trichloroethane (Methyl Chloroform)	ND< 6.5 #			ND< 13 #		ND< 5.1 #	ND< 5.8 #
1,1,2-Trichloroethane	ND< 6.5 #			ND< 2.2 #		ND< 4.9 #	4.9 BU
1,1,2,2-Tetrachloroethane	ND< 6.5 #			ND< 10 #		ND< 5.1 #	ND< 5.8 #
1,1-Dichloroethene	ND< 6.5 #			ND< 12 #		ND< 5.1 #	ND< 5.8 #
cis-1,2-Dichloroethene				ND< 3.1 #			
Trans-1,2-Dichloroethene (Ethylene	ND< 6.5 #			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
Tetrachloroethene	ND< 6.5 #	0.56 BU		ND< 3.1 BN		3.1 B	ND< 5.8 #
Trichloroethene	ND< 6.5 #			ND< 3.1 #		ND< 5.1 #	ND< 5.8 #
Chloromethyl Methyl Ether				ND< 13 #			
2-Chloroethylvinylether	ND< 6.5 #					ND< 5.1 #	ND< 5.8 #
Vinyl Chloride	ND< 6.5 #			ND< 10 #		ND< 5.1 #	ND< 5.8 #
Vinyl Acetate	ND< 6.5 #	0.43 BU		ND< 4.5 #		ND< 5.1 #	ND< 5.8 #
1,2-Dibromo-3-chloropropane	ND< 6.5 #			ND< 12 #			
1,2-Dichloropropane (Propylene Dichloride)				ND< 1.8 #		ND< 5.1 #	ND< 5.8 #
Methyl Methacrylate		1.1 BU		ND< 2.4 #			
Ethyl Acrylate				ND< 2.6 #			
3-Chloropropylene	ND< 6.5 #						
cis-1,3-Dichloropropene	ND< 6.5 #			ND< 1.8 #		ND< 5.1 #	ND< 5.8 #

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC), (continued)

	Coal Creek	Boswell	Springerville	Cardinal	Baldwin	Niles	SNOX
Units: lb/10^{12} Btu				Non Soot			
trans-1,3-Dichloropropene				ND< 6.9 #		ND< 5.1 #	ND< 5.8 #
1,2-Epoxybutane	41			ND< 7.6 #			
1,3-Butadiene				ND< 18 #			
2-Chloro-1,3-Butadiene (Chloroprene)				ND< 41 #			
n-Hexane		1.5 U		6.5 A	0.16 U		
2,2,4-Trimethylpentane				ND< 1.6 #			
Benzene		100 U	170 N	3.4 A	120 U	7.9	5.6
1,2,4-Trimethylbenzene	ND< 6.5 #						
1,3,5-Trimethylbenzene	3.3 B						
Ethyl Benzene		0.43 U		ND< 2.2 #	0.13 BU	ND< 5.1 #	ND< 5.8 #
Styrene	3.3 B	1.8 U		ND< 3.1 #	0.20 AU	ND< 5.1 #	ND< 5.8 #
Iso-propyl Benzene (Cumene)		0.30 U		ND< 3.0 #			
Chlorobenzene		0.16 BU		ND< 2.2 #		ND< 5.1 #	ND< 5.8 #
1,2-Dichlorobenzene				ND< 3.1 #			
1,3-Dichlorobenzene	24			ND< 3.1 #			
1,4-Dichlorobenzene				ND< 3.1 #			
1,2,4-Trichlorobenzene	3.5 A						
Toluene		5.7	3.6 N	5.2 U	2.0 U	3.5 BU	3.9 AU
4-Ethyl Toluene							
Xylenes						ND< 5.1 #	ND< 5.8 #
m,p-Xylenes		2.2	0.65 BN	3.0 AU	0.97 U		
o-Xylene		0.28 U		ND< 3.1 #	0.52		
Methyl Hydrazine				6.6 BU			
Methyl tert-Butyl Ether				1.4 B			
Acrylonitrile				ND< 12 #			
Allyl Chloride				ND< 12 #			
Propylene Oxide				ND< 12 #			

ND< Value shown is detection limit.
\# Of the calculations contributing to the average value shown, all include a non-detect measurement.
A Of the calculations contributing to the average value shown, one includes a non-detect measurement.
B Of the calculations contributing to the average value shown, two include a non-detect measurement.
C Of the calculations contributing to the average value shown, more than two include a non-detect measurement.
U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC), (continued)

	Yates	Bailly	Nelson Dewey		Hammond		Smith	
			Baseline	Reburn	OFA	LNB	Baseline	Low NO_x
Units: $lb/10^{12}$ Btu								
Carbon Disulfide	2.2					ND< 0.51		
Bromomethane (Methyl Bromide)					ND< 0.49 #	0.72 BU		
1,2-Dibromomethane								
Bromodichloromethane								
Dibromochloromethane								
Dibromoethane (Ethylene Dibromide)								
Tribromomethane (Bromoform)								
Chloromethane								
Dichloromethane (Methylene Chloride)					3.8 AU	14 U		
Trichlorofluoromethane								
Trichloromethane (Chloroform)								
Carbon Tetrachloride								
Iodomethane								
Bromoethene								
Chloroethane (Ethyl Chloride)								
1,1-Dichloroethane (Ethylidene Dichloride)								
1,2-Dichloroethane								
1,1,1-Trichloroethane (Methyl Chloroform)					ND< 0.49 #			
1,1,2-Trichloroethane								
1,1,2,2-Tetrachloroethane								
1,1-Dichloroethene								
cis-1,2-Dichloroethene								
Trans-1,2-Dichloroethene (Ethylene Dichloride)								
Tetrachloroethene								
Trichloroethene								
Chloromethyl Methyl Ether								
2-Chloroethylvinylether								
Vinyl Chloride								
Vinyl Acetate								
1,2-Dibromo-3-chloropropane								
1,2-Dichloropropane (Propylene Dichloride)								
Methyl Methacrylate								
Ethyl Acrylate								

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC), (continued)

	Yates	Bailly	Nelson Dewey		Hammond		Smith	
			Baseline	Reburn	OFA	LNB	Baseline	Low NO_x
Units: lb/10^{12} Btu								
3-Chloropropylene								
cis-1,3-Dichloropropene								
trans-1,3-Dichloropropene								
1,2-Epoxybutane								
1,3-Butadiene								
2-Chloro-1,3-Butadiene (Chlorprene)								
n-Hexane								
2,2,4-Trimethylpentane								
Benzene	1.3		2.0 N	0.59 N	1.4 U	ND< 0.51	920 N	1000 N
1,2,4-Trimethylbenzene								
1,3,5-Trimethylbenzene								
Ethyl Benzene							59 N	
Styrene							19 N	
Iso-propyl Benzene (Cumene)								
Chlorobenzene								
1,2-Dichlorobenzene							ND< 3.7 #	ND< 3.7 #
1,3-Dichlorobenzene								
1,4-Dichlorobenzene							ND< 3.7 #	ND< 3.7 #
1,2,4-Trichlorobenzene							ND< 4.3 #	ND< 4.5 #
Toluene	2.0		1.1 N	1.2 N	ND< 0.49 #	0.7	17 N	5.5 N
4-Ethyl Toluene								
Xylenes							3.6 N	
m,p-Xylenes								
o-Xylene								
Methyl Hydrazine								
Methyl tert-Butyl Ether								
Acrylonitrile								
Allyl Chloride								
Propylene Oxide								

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N Uncertainty limit not known or not calculated.

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC), (continued)

	Burger		Arapahoe		TIDD	AirPol (Shawnee)		
	Baseline	SNRB	Baseline	SNCR		GSA+ESP	GSA+FF	GSA+ESP+FF
Units: lb/10^{12} Btu								
Carbon Disulfide					1.0			
Bromomethane (Methyl Bromide)					ND< 0.7 BN			
1,2-Dibromomethane	7.0 N	4.4 BU						
Bromodichloromethane					ND< 0.7 BN			
Dibromochloromethane					ND< 0.7 N			
Dibromoethane (Ethylene Dibromide)								
Tribromomethane (Bromoform)					ND< 0.7 #			
Chloromethane					4.4 B			
Dichloromethane (Methylene Chloride)	ND< 1.6 #	410. BU			3.6			
Trichlorofluoromethane					ND< 0.7 N			
Trichloromethane (Chloroform)	7.9 N	ND< 2.5 #			ND< 0.7 BN			
Carbon Tetrachloride					ND< 0.7 N			
Iodomethane								
Chloroethane (Ethyl Chloride)					ND< 0.7 BN			
1,1-Dichloroethane (Ethylidene Dichloride)	10. N	ND< 2.1 AN						
1,2-Dichloroethane					8.7			
1,1,1-Trichloroethane (Methyl Chloroform)	3.4 N	ND< 2.8 BN			16			
1,1,2-Trichloroethane								
1,1,2,2-Tetrachloroethane								
1,1-Dichloroethene								
trans-1,2-Dichloroethene (Ethylene Dichloride)					ND< 0.7 N			
Tetrachloroethene					ND< 0.7 N			
Trichloroethene					ND< 0.7 N			
2-Chloroethylvinylether								
Vinyl Chloride					ND< 0.7 N			
Vinyl Acetate, lb/10^{12} Btu					ND< 3.3 N			
1,2-Dichloropropane (Propylene Dichloride)								
Methyl Methacrylate								
3-Chloropropylene	9.5 N	8.3 AU						
cis-1,3-Dichloropropene	6.5 N	ND< 2.3 BN			ND< 0.7 N			
trans-1,3-Dichloropropene	ND< 2.0 #	2.5 BU			ND< 0.7 N			

Table 2-5.4 Emission Factors, Volatile Organic Compounds (VOC), (continued)

	Burger		Arapahoe		TIDD	AirPol (Shawnee)		
	Baseline	SNRB	Baseline	SNCR		GSA+ESP	GSA+FF	GSA+ESP+FF
Units: lb/10^{12} Btu								
n-Hexane								
Benzene	26 N	7.0 U	2.6		6.6	2.6		
1,2,4-Trimethylbenzene	ND< 2.2 #	ND< 2.5 #						
1,3,5-Trimethylbenzene	6.2 N	ND< 2.5 #						
Ethyl Benzene	29 N	9.5 BU			ND< 0.7 N			
Styrene	ND< 1.9 #	6.2 BU			ND< 0.7 N			
Iso-propyl Benzene (Cumene)								
Chlorobenzene					ND< 0.7 N			
1,3-Dichlorobenzene	260 N	19 BU						
1,4-Dichlorobenzene	360 N	27 BU						
1,2,4-Trichlorobenzene	230 N	83 BU						
Toluene	ND< 1.7 #	ND< 1.9 BN	105		1.4	105		
Benzyl Chloride	110 N	19 BU						
4-Ethyl Toluene	6.2 N	ND< 2.5 #						
Xylenes								
m,p-Xylenes	4.3 N	8.4 BU			ND< 0.7 N			
o-Xylene	3.1 N	ND< 2.2 #			ND< 0.7 N			
Methyl Hydrazine								
Methyl tert-Butyl Ether								

ND< Value shown is detection limit.
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N Uncertainty limit not known or not calculated.

Table 2-5.5 Emission Factors, Semi-Volatile Organic Compounds (SVOC)

	Coal Creek	Boswell	Springerville	Cardinal	Baldwin	Niles	SNOX
Units: lb/10^{12} Btu							
Acetophenone	0.54 U	0.71		ND< 140 BN	1.2	0.64 U	0.30 U
2-Chloroacetophenone	0.13			ND< 54 #		0.29 U	ND<0.0055 #
Biphenyl	0.023	ND<0.18 #		ND< 5.6 BN	ND<0.88 #	0.13 U	0.0060 AU
Dibenzofuran	0.052			ND< 22 #		0.065 U	0.013
2,4-Dinitrotoluene	0.0065 AU			ND< 22 #		0.020 AU	0.0038 B
2,6-Dinitrotoluene	ND<0.0017 #			ND< 22 #		0.55	ND<0.0055 #
Isophorone				23 BU	26 U		
Quinoline	ND<0.017 #			ND< 5.6 BN			
Hexachloroethane	ND<0.0017 #			ND< 22 #		ND<0.012 #	ND<0.0055 #
Bis(2-Chloroisopropyl) Ether							
n-Nitrosodimethylamine		ND<0.89 #		ND< 22 #			
Phenol		0.43 A		ND< 22 #	ND<1.2 A		
2-Nitrophenol				ND< 22 #			
Benzyl Chloride	0.0057 BU			87 N		ND<0.012 #	0.025 AU
Hexachlorobenzene	ND<0.0017 #			ND< 22 #		ND<0.012 #	ND<0.0055 #
Hexachloroethane				ND< 22 #			
Hexachlorobutadiene	ND<0.0017 #			ND< 22 #		ND<0.012 #	ND<0.0055 #
Hexachlorocyclopentadiene	ND<0.0017 #			ND< 22 #		ND<0.012 #	ND<0.0055 #
2-Methylphenol (o-Cresol)		1.0 AU		ND< 22 #	1.8 BU		
4-Methylphenol (p-Cresol)		0.65 AU		ND< 22 #	0.78 BU		
Pentachlorophenol	ND<0.0017 #			ND< 54 #		ND<0.012 #	0.0032 B
Benzoic Acid							
Benzyl Alcohol							
Butylbenzylphthalate				ND< 22 #			
Dibutylphthalate		ND<1.9 #		ND< 22 #	ND<3.0 B		
Diethylphthalate				ND< 22 #			
Dimethylphthalate				ND< 22 #			
Bis(2-Ethylhexyl)phthalate		ND<1.7 B		ND< 22 #	4.6 U		
Dimethyl Sulfate				1.8 BU			
Total SVOCs, PAHs							

ND< Value shown is detection limit.
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N Uncertainty limit not known or not calculated.

Table 2-5.5 Emission Factors, Semi-Volatile Organic Compounds (SVOC), (continued)

	Yates	Bailly	Nelson Dewey		Hammond		Smith	
			Baseline	Reburn	OFA	LNB	Baseline	Low NO_x
Units: $lb/10^{12}$ Btu								
Acetophenone	3.2							
2-Chloroacetophenone								
Biphenyl								
Dibenzofuran							ND< 3.7 #	ND< 3.7 #
2,4-Dinitrotoluene							ND< 2.2 #	ND< 2.2 #
2,6-Dinitrotoluene								
Isophorone							ND< 3.7 #	ND< 3.7 #
Quinoline								
Hexachloroethane								
Bis(2-Chloroisopropyl) Ether								ND< 1.5 #
n-Nitrosodimethylamine								
Phenol	9.2				5.5 BU		29. BN	18. N
2-Nitrophenol								5.4 N
Benzyl Chloride								
Hexachlorobenzene							ND< 5.8 #	ND< 6.0 #
Hexachloroethane							ND< 2.2 #	ND< 2.2 #
Hexachlorobutadiene							ND< 2.2 #	ND< 2.2 #
Hexachlorocyclopentadiene							ND< 3.7 #	ND< 3.7 #
2-Methylphenol (o-Cresol)	2.9 U							
4-Methylphenol (p-Cresol)	0.95 AU							
Pentachlorophenol							ND< 5.8 #	ND< 6.0 #
Benzoic Acid	120						61. N	37. CN
Benzyl Alcohol	2.8 BU							
Butylbenzylphthalate								
Dibutylphthalate					ND< 4.8 #			
Diethylphthalate								
Dimethylphthalate							ND< 2.2 #	ND< 2.2 #
Bis(2-Ethylhexyl)phthalate					6.2 AU			
Dimethyl Sulfate								
Total SVOCs, PAHs								

ND< Value shown is detection limit.
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N Uncertainty limit not known or not calculated.

Table 2-5.5 Emission Factors, Semi-Volatile Organic Compounds (SVOC), (continued)

	Burger		Arapahoe		TIDD	AirPol (Shawnee)		
	Baseline	SNRB	Baseline	SNCR		GSA+ESP	GSA+FF	GSA+ESP+FF
Units: lb/10^{12} Btu								
Acetophenone					3.9			
2-Chloroacetophenone								
Biphenyl	0.0030	0.012						
Dibenzofuran								
2,4-Dinitrotoluene								
2,6-Dinitrotoluene								
Isophorone					21 AU			
Quinoline								
Hexachloroethane								
Bis(2-Chloroisopropyl) Ether								
n-Nitrosodimethylamine								
Phenol					1.2 CU			
2-Nitrophenol								
Benzyl Chloride	110	19						
Hexachlorobenzene								
Hexachloroethane								
Hexachlorobutadiene								
Hexachlorocyclopentadiene								
2-Methylphenol (o-Cresol)								
4-Methylphenol (p-Cresol)								
Pentachlorophenol								
Benzoic Acid					160			
Benzyl Alcohol								
Butylbenzylphthalate								
Dibutylphthalate								
Diethylphthalate								
Dimethylphthalate								
Bis(2-Ethylhexyl)phthalate								
Dimethyl Sulfate								
Total SVOCs, PAHs								

ND< Value shown is detection limit.
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N Uncertainty limit not known or not calculated.

Table 2-5.6 Emission Factors, Polynuclear Aromatic Hydrocarbons (PAH)

	Coal Creek	Boswell	Springer-ville	Cardinal	Baldwin	Niles	SNOX
Units: lb/10^{12} Btu							
Acenaphthylene	0.01 U	0.0053 U		ND<22 #	0.032 U	0.0068 AU	0.0042 U
Acenaphthene	0.017 U	0.041 U		ND<22 #	ND<0.0063 #	0.027 U	0.0053 U
Anthracene	0.015	0.0062 U		ND<22 #	ND<0.0026 AU	0.021 U	0.0036 U
Benzo(a)anthracene	0.0021	0.0047 U		ND<22 #	ND<0.0012 #	0.0037 AU	0.0021
Benzo(b & k)anthracene							
Benzo(b & k)fluoranthene	0.0045			ND<22 #		0.007 AU	0.0039
Benzo(b) fluoranthene		0.0027 U		ND<22 #	ND<0.0026 #		
Benzo(k)fluoranthene		0.00033 U		ND<22 #	ND<0.0013 BU		
Benzo(e)pyrene	0.0011	0.0023 U			ND<0.0017 #	0.0021 BU	0.0011 BU
Chrysene	0.0053 U	0.012 U		ND<22 #	ND<0.0021 B	0.0089 U	0.0021 AU
5-Methyl Chrysene							
Naphthalene	0.25	0.23 AU	ND< 0.12 N	1.9 U	ND<0.39 AU	0.22 U	0.060 U
1-Methylnaphthalene	0.015					0.016 U	0.011 U
2-Methylnaphthalene	0.041	0.032		ND<22 #	ND<0.034 B	0.038 U	0.020 U
2-Chloronaphthalene		0.00063		ND<22 #	0.00035 U		
Fluoranthene	0.042	0.083 U		ND<22 #	0.017 U	0.027 U	0.0069
Fluorene	0.042 U	0.0088 U		ND<22 #	ND<0.0049 B	0.031 U	0.00060 BU
Phenanthrene	0.31 U	0.21 U		ND<22 #	0.057	0.078 U	0.024 U
Pyrene	0.016	0.037 U		ND<22 #	ND<0.0028 BU	0.014 U	0.0012 AU
Benzo(g,h,i)perylene	0.00059 AU	ND<0.00052 #		ND<22 #	ND<0.0011 #	ND<0.0024 #	0.00093 B
Benzo(a)pyrene	0.00086 AU	ND<0.00021 B		ND<22 #	ND<0.00054 #	ND<0.0024 #	0.00094 B
Dibenzo(a,h)anthracene	0.00072	ND<0.00012 B		ND<22 #	ND<0.00029 #	ND<0.0024 #	0.00071 B
Indeno(1,2,3-c,d)pyrene	0.00063 AU	ND<0.00034 BU		ND<22 #	ND<0.0011 #	ND<0.0024 #	0.0010 BU
Perylene		0.08 BU			ND<0.00027 #		
17H-Dibenzo(c,g)carbazole							
Dibenzo(a,e)pyrene							
Dibenzo(a,j)pyrene							
Dibenzo(a,h)acridine							
Dibenzo(a,j)acridine							

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N Uncertainty limit not known or not calculated.

Table 2-5.6 Emission Factors, Polynuclear Aromatic Hydrocarbons, (continued)

	Yates	Bailly	Nelson Dewey		Hammond		Smith	
			Baseline	Reburn	OFA	LNB	Baseline	Low NO_x
Units: lb/10^{12} Btu								
Acenaphthylene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0030		
Acenaphthene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0081		
Anthracene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0037 U		
Benz(a)anthracene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0070 U		
Benz(b & k) anthracene								
Benzo(b & k) fluoranthene						0.0015 U		
Benzo(b)fluoranthene			ND< 9.0 #	ND< 12 #				
Benzo(k)fluoranthene			ND< 9.0 #	ND< 12 #				
Benzo(e) pyrene								
Chrysene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0018 U		
5-Methyl Chyrsene						ND<0.0009 BN		
Naphthalene	1.5		ND< 9.0 #	ND< 12 #			ND< 2.2 #	ND< 1.5 #
1-Methylnaphthalene								
2-Methylnaphthalene								ND< 1.5 #
2-Chloronaphthalene								
Fluoranthene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.01 U		
Fluorene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.0099 U		
Phenanthene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.044 U		
Pyrene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	0.011 U		
Benzo(g,h,i)perylene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	ND<0.0031 BN		
Benzo(a)pyrene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	ND<0.0041 BN		
Dibenzo(a,h)anthracene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	ND<0.0037 #		
Indeno(1,2,3-c,d)pyrene			ND< 9.0 #	ND< 12 #	ND< 5.0 #	ND<0.0027 AN		
Perylene								
17H-Dibenzo(c,g)carbazole						ND<0.016 #		
Dibenzo(a,e)pyrene						ND<0.0030 #		
Dibenzo(a,h)pyrene						ND<0.0032 #		
Dibenzo(a,i)pyrene						ND<0.0042 #		
Dibenzo(a,h)acridine						ND<0.0016 #		
Dibenzo(a,i)acridine						ND<0.0042 #		

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N Uncertainty limit not known or not calculated.

Table 2-5.6 Emission Factors, Polynuclear Aromatic Hydrocarbons, (continued)

	Burger (116)		Arapahoe (PSC CO)		TIDD	AirPol (Shawnee)		
	Baseline	SNRB	Baseline	SNCR		GSA+ESP	GSA+FF	GSA+ESP+FF
Units: lb/10^{12} Btu								
Acenaphthylene	0.0032 U	0.0024 U			0.12			
Acenaphthene	0.0078 U	0.011 AU						
Anthracene	0.0068	0.0088 U						
Benz(a)anthracene	0.013 U	0.0084						
Benz(b & k)anthracene								
Benzo(b & k)fluoranthene	0.019 U	0.021						
Benzo(b)fluoranthene								
Benzo(k)fluoranthene								
Benzo(e)pyrene	0.0074	0.0082 U						
Chrysene	0.043 U	0.015						
5-Methyl Chyrsene								
Naphthalene	0.061 U	0.4 U	0.26					
1-Methylnaphthalene	0.0029	0.011 U						
2-Methylnaphthalene	0.0073	0.022 U	0.027 U					
2-Chloronaphthalene					0.0012			
Fluoranthene	0.066	0.068 U						
Fluorene	0.017	0.063 U						
Phenanthrene	0.11 U	0.15 U						
Pyrene	0.031	0.028 U						
Benzo(g,h,i)perylene	0.009	0.012 U						
Benzo(a)pyrene	0.02 U	0.012						
Dibenzo(a,h)anthracene	0.0061	0.0096 U						
Indeno(1,2,3,-c,d)pyrene	0.009 U	0.011 U						
Perylene								
17H-Dibenzo(c,g)carbazole								
Dibenzo(a,e)pyrene								
Dibenzo(a,h)pyrene								
Dibenzo(a,i)pyrene								
Dibenzo(a,h)acridine								
Dibenzo(a,i)acridine								

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N Uncertainty limit not known or not calculated.

Table 2-6.1 Emission Factors, Trace Metals

Plants	Coal Creek	Boswell	Springer-ville	Cardinal		Baldwin		Niles	SNOX	Yates
				Non-Soot Blowing	Soot Blowing	Non-Soot Blowing	Soot Blowing			
Units: lb/10^{12} Btu										
Antimony	0.18	ND< 0.68 #	0.040 AU	2.4 AN	1.4 CN	1.5	2.1	ND< 0.36 #	ND< 0.50 #	0.06
Arsenic	1.2	ND< 0.32 B	0.14 BU	3.5 CN	1.7 AN	13 U	12	42.	ND< 0.50 #	1.2
Barium	160	82 U	13	0.89 N	0.59 BN	5.3	3.4	5.4 U	0.17 BU	2.8 AU
Beryllium	ND< 1.7 #	ND< 0.13 #	ND< 0.04 #	0.067 CN	0.038 CN	1.4	1.7	0.19	0.17 AU	0.10 AU
Boron	19 U	610 U	580	1,910 BN	1,750 N	7,700	8,600			
Cadmium	ND< 3.2 #	ND< 0.65 #	0.026 U	0.85 N	0.66 N	3.0	4.5	0.07 BU	0.092 BU	0.60 AU
Chromium	10 N	2.0	0.10 BU	7.5 N	2.2 N	51	68	3.0	3.9 N	5.3 AU
Cobalt	1.5 BU	0.70	ND< 0.3 #	0.63 N	0.31 CN	6.8	10	ND< 0.12 #	ND< 0.22 BN	0.70 U
Copper	1.5 AN	2.4	0.93	1.4 N	1.1 N	19 U	33	4.0	0.89	2.0 U
Lead	0.69	2.4 AU	0.67	3.8 N	3.6 N	29	48	1.6	0.53 BU	0.60 AU
Manganese	30	18 U	11	15 N	20 N	22	32	3.4	2.6 U	7.2 U
Mercury	9.5	1.9	4.0	0.44 CN	0.78 CN	3.8	5.4	14.	22.	3.0
Molybdenum	0.51 N	1.3 U	1.4	0.59 CN	0.27 CN	34	41	2.3	5.4	1.5 U
Nickel	5.1 N	2.0 U	ND< 0.3 #	4.8 N	1.8 N	22	31	0.55 U	2.2 N	40. U
Selenium	8.3	3.2	ND< 0.038 BN	93 N	65 N	130	140 U	62. U	0.67 U	27 U
Vanadium	4.4	1.5 U	1.0 U	1.6 CN	0.72 CN	100	220 U	2.5	ND< 0.11 #	2.1

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C Of the calculations contributing to the average value shown, more than two include a non-detect measurement.
U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-6.1 Emission Factors, Trace Metals, (Continued)

Plants	Bailly	Nelson-Dewey		Hammond		Smith		Burger	
		Baseline	Reburn	OFA	LNB	Baseline	Low NOx	Baseline	SNRB
Units: lb/10^{12} Btu									
Antimony	0.28 U			ND< 25 #	23 C	ND< 7.6 #	2.2 CN	0.10	0.76 U
Arsenic	1.1 U	7.9 N	8.6 N	94. U	110	1.1 N	9.6 N	2.9 U	1.2 U
Barium	1.3			220	140	3.7 N	19 N	1.2 BU	0.18 AU
Beryllium	ND< 0.07 AN	2.4 N	1.0 N	3.7 U	3.1	ND< 0.53 #	ND< 0.60 #	ND< 13 #	ND< 15 #
Boron	910.								
Cadmium	0.42	2.8 N	1.7 N	0.50 U	3.6	0.99 AN	ND< 2.2 CN	ND< 13 #	0.64 AU
Chromium	2.7	15. N	5.2 N	38	21	8.2 N	22 N	1.0 AU	5.3 AU
Cobalt	ND< 0.07 AN			11. U	6.5	4.9 BN	43 N	ND< 16 #	ND< 18 AN
Copper	1.7 U			41. U	30	4.4 N	1.0 BN		
Lead	1.6 U	92. N	59. N	33. U	11	7.6 N	16 N	ND< 0.22 BN	0.53 AU
Manganese	3.1	22. N	16. N	25.	21	5.0 N	105 N	10 U	0.81 AU
Mercury	2.1	4.9 N	4.0 N	6.4	4.8	0.07 N	0.40 N	9.2	14 U
Molybdenum	3.4			ND< 12 B	12	5.7 BN	35 N		
Nickel	2.2	82. N	35. N	24.	17	5.5 AN	7.4 N	ND< 16 #	49 AU
Selenium	190 U	250. N	150. N	130.	140	14 N	27 N	31 U	ND< 0.32 #
Vanadium	2.8			72.	41	12 AN	37 N	ND< 14 AN	ND< 16 #

ND< Value shown is detection limit.
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U Uncertainty (= 95% Confident Limit): Equal to or greater than 100 percent of value.
N Uncertainty limit not known or not calculated.

Table 2-6.1 Emission Factors, Trace Metals, (Continued)

Plants	Arapahoe		TIDD	AirPol GSA (Shawnee)					
				No Lime Injection (Baseline)			Lime Injection (Demonstration)		
	Baseline	SNCR		Parallel ESP	Parallel FF	Series ESP+FF	Parallel ESP	Parallel FF	Series ESP+FF
Units: lb/10^{12} Btu									
Antimony			ND< 2.6 #	ND< 0.058 #	ND< 0.075 #	ND< 0.071 #	ND< 0.062 #	ND< 0.062 #	ND< 0.058 #
Arsenic	0.75 U	0.15	1.2	5.1	0.71	0.07 BU	14 U	0.08 BU	ND< 0.041 #
Barium	1.1 U	1.1 U	0.92	ND< 3.2 #	ND< 4.1 #	ND< 3.9 #	47 U	ND< 3.4 #	ND< 3.2 #
Beryllium	ND< 0.02 #	ND< 0.02 #	0.26 B						
Boron			210				0.42 U		0.22 A
Cadmium	0.12 AU	ND< 0.07 #	2.2	0.86	2.2	0.47	20 AU	1.4	ND< 1.9 #
Chromium	0.66	0.30	4.6	6.4	ND< 2.4	ND< 2.2 #	4.5 AU	ND< 2.0 #	ND< 0.82 #
Cobalt	ND< 0.21 #	ND< 0.23 #	ND< 2.4 #	1.1	ND< 1.1 #	ND< 1.0 #		ND< 0.88 #	
Copper	1.1	1.3	5.3				13 U		0.27
Lead	0.44	0.4	0.80 B	3.8	0.94	0.61	26 U	0.59 U	1.4
Manganese	1.0 U	0.89 U	8.5	8.7 U	3.2	2.2 U	1.3	5.1 U	0.12 AU
Mercury	ND< 0.29 #	0.41 AU	18	0.46	1.1 AU	0.11 U		0.74 U	
Molybdenum	0.17	0.27 U	0.31 A						
Nickel	1.5 U	0.45	7.4				ND< 0.047 #	ND< 0.047 #	ND< 0.044 #
Selenium	0.36 U	ND< 0.060 #	49	13 U	ND< 0.057 #	1.2 U	42 AU	ND< 6.6 #	ND< 6.2 #
Vanadium	0.24 U	0.29	1.2	ND< 6.1 BU	ND< 7.9 #	ND< 7.5 #			

ESP Electrostatic Precipitator
FF Fabric Filter
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N Uncertainty limit not known or not calculated.

Table 2-6.2 Emission Factors, Inorganics

Plants	Coal Creek	Boswell	Springer-ville	Cardinal		Baldwin	Niles	SNOX	Yates
				Non-Soot Blowing	Soot Blowing				
Units: lb/10^{12} Btu									
Anions									
Chloride (HCl)	1,340	1,100	ND< 176 BN	24,400 N		78,000	132,000	82,400	742
Fluoride (HF)	4,126	2,800	ND< 92 #	1,900 N		9,500	8,930	6,800	122
Phosphates	7.8 AU			ND< 920 BN			111 AU	ND< 2.0 BU	
Sulfates	1,220 U			800,000 N			12,280	56,600. U	
Reduced Species									
Ammonia	ND< 3.7 #	ND< 17 B		41 N		ND< 17 B	70 BU	56 N	
Cyanide	51	3.7 U		ND< 0.59 #		ND< 2.2 #	180 U	157	

Plants	Bailly	Nelson-Dewey		Hammond		Smith		Burger	
		Baseline	Reburn	OFA	LNB	Baseline	Low NOx	Baseline	SNRB
Units: lb/10^{12} Btu									
Anions									
Chloride (HCl)	1,020.	4,500. N	6,100. N	19,000	15,000	150,000. N	170,000. N	33,000	770 U
Fluoride (HF)	ND< 420. #	67. N	89. N	6,200	5,100	4,700. N	4,000. N	5,500	39 U
Phosphates	ND< 2,200. #					ND< 95. #	160. N		
Sulfates	590,000. N								
Reduced Species									
Ammonia									
Cyanide									

Table 2-6.2 Emission Factors, Inorganics (Continued)

Plants	Arapahoe (PSC Colorado)		TIDD	AirPol GSA (Shawnee)					
				No Lime Injection (Baseline)			Lime Injection (Demonstration)		
	Baseline	SNCR		ESP	FF	ESP+FF	ESP	FF	ESP+FF
Units: lb/10^{12} Btu									
Anions									
Chloride (HCl)	630	720	83,000		18,140	18,440		ND< 7.3 #	ND< 210. #
Fluoride (HF)	4,300 U	4,800	5,600		1,530	4,210		ND< 23. #	ND< 21. #
Phosphates									
Sulfates									
Reduced Species									
Ammonia		4,300-8,900	140						
Cyanide	ND< 8 BN	ND< 9 #	610						

ESP Electrostatic Precipitator
FF Fabric Filter
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N Uncertainty limit not known or not calculated.

Table 2-7 Stack Concentrations

	Coal Creek	Boswell	Springerville	Cardinal		Baldwin		Niles	SNOX	Yates
				Non-Soot Blowing	Soot Blowing	Non-Soot Blowing	Soot Blowing			
Units: µg/Nm³										
Antimony	0.25 N	ND< 0.91 #	0.058 AN	3.1 A	1.8 C	2.1	2.8	ND< 0.60 #	ND< 0.69 #	0.065
Arsenic	1.7 N	ND< 0.44 BU	0.21 BN	4.5 C	2.2 A	18	17	70 N	ND< 0.69 #	1.2
Barium	217 N	110 N	20 N	1.1	0.75 B	7.2	4.6	8.8 N	0.24 BN	2.9 AU
Beryllium	ND< 2.3 #	ND< 0.17 #	ND< 0.05 #	0.09 C	0.049 C	1.9	2.3	0.31 N	0.23 AN	0.099 AU
Boron	26 N	800 N	865 N	2,470 B	2,250	10,000	12,000		--	440
Cadmium	ND< 4.3 #	ND< 0.86 #	0.037 N	1.1	0.86	4.1	6	ND< 0.10 BN	ND< 0.16 BN	0.63 AU
Chromium	13 N	2.7 N	0.15 BN	9.8	2.8	69	92	5.1 N	5.4 N	5.4 AU
Cobalt	ND< 2.2 BN	0.93 N	ND< 0.4 #	0.82	0.39 C	9.3	13	ND< 0.20 #	ND< 0.30 BN	0.74 U
Copper	ND< 2.7 AN	3.2 N	1.4 N	1.8	1.4	26	44	6.7 N	1.2 N	2.0
Lead	0.92 N	3.2 AN	1.0 N	5.0	4.6	39	64	2.7 N	0.73 BN	0.61 A
Manganese	40 N	25 N	16 N	19	26	30	43	5.6 N	3.6 N	7.3 U
Mercury	13 N	2.6 N	9.64 N	0.56 C	1.0 C	5.2	7.2	24 N	30 N	3.1
Molybdenum	0.68 N	1.7 N	2.04 N	0.76 C	0.35 C	46	56	3.7 N	7.5 N	1.5 U
Nickel	6.9 N	2.6 N	ND< 0.4 #	6.2	2.3	30	42	0.90 N	3.0 N	41 U
Selenium	11 N	4.3 N	ND< 0.054 BN	120	83	180	190	102 N	0.92 N	27 U
Vanadium	5.9 N	2.0 N	1.5 N	2.1 C	0.92 C	140	300	4.2 N	ND< 0.15 #	2.2

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N Uncertainty limit not known or not calculated.

Table 2-7 Stack Concentrations, (continued)

	Bailly	Nelson-Dewey		Hammond		Smith		Burger	
		Baseline	Reburn	OFA	OFA/LNB	Baseline	Low NOx	Baseline	SNRB
Units: µg/Nm³									
Antimony	0.38 N			ND< 29 #	2.6	ND< 25 #	5.6 CN	0.13	0.82 U
Arsenic	1.4 N	11	12	110 U	120	1.8 N	13 N	3.6 U	1.3 U
Barium	1.7 N			260	160	5.6 N	25 N	1.4 BU	0.20 AU
Beryllium	ND< 0.10 AN	3.6	1.3	4.3 U	3.5	ND< 1.4 #	ND< 1.3 #	ND< 16 #	ND< 16 #
Boron	1,230 N								
Cadmium	0.57 N	4.0	2.4	0.59 U	4.2	1.4 AN	ND< 4.0 CN	ND< 16 #	0.68 AU
Chromium	3.7 N	21	7.4	44	24	18 N	41 N	1.3 AU	5.6 AU
Cobalt	ND< 0.10 AN			13 U	7.5	8.6 BN	4.0 N	ND< 19 #	ND< 19 AN
Copper	2.3 N			48	35	14 N	6.5 BN		
Lead	2.1 N	130	78	39	13	21 N	23 N	ND< 0.27 BN	0.56 AU
Manganese	4.2 N	31	23	29	24	71 N	21 N	13 U	0.86 AU
Mercury	2.8 N	6.9	5.7	7.5	5.5	0.76 N	0.97 N	11	15. U
Molybdenum	4.6 N			ND< 14 CN	14	2.3 BN	41 N		
Nickel	2.9 N	120	50	28	19	12 AN	8.3 N	ND< 19 #	52. A
Selenium	261. N	360	220	150	160	64 N	170 N	38 U	ND< 0.34 #
Vanadium	3.8 N			84	47	16 AN	1.4 N	ND< 17 AN	ND< 17 #

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Table 2-7 Stack Concentrations, (continued)

	Arapahoe		TIDD	AirPol GSA					
				No Lime Injection (Baseline)			Lime Injection (Demonstration)		
	Baseline	SNCR		Parallel ESP	Parallel FF	Series ESP+FF	Parallel ESP	Parallel FF	Series ESP+FF
Units: µg/Nm³									
Antimony			ND< 2.1 #	ND< 0.09 #	ND< 0.10 #	ND< 0.095 #	ND< 0.09 #	ND< 0.09 #	ND< 0.079 #
Arsenic	0.97 U	0.19	1.0	8.2	0.98	ND< 0.090 BU	19 U	0.12 BU	ND< 0.056 #
Barium	1.5 U	1.3 U	0.74 U	ND< 5.1 #	ND< 5.6 #	ND< 5.2 #	66 U	ND< 4.7 #	ND< 4.3 #
Beryllium	ND< 0.03 #	ND< 0.03 #	0.021 BU						
Boron			170						
Cadmium	0.15 AU	ND< 0.09 #	1.8 U	1.4	3.0	0.63	0.59 U	1.9	0.30 A
Chromium	0.85	0.37	3.7 U	10	ND< 3.3 #	ND< 3.0 #	27 AU	ND< 2.7 #	ND< 2.5 #
Cobalt	ND< 0.28 #	ND< 0.29 #	ND< 0.19 #	1.8	ND< 1.5 #	ND< 1.3 #	6.2 AU	ND< 1.2 #	ND< 1.1 #
Copper	1.4	1.7	4.1 U						
Lead	0.56	0.50	0.65 BU	6.2	1.3	0.82	18 U	0.82 U	0.37
Manganese	1.3 U	1.1 U	6.9 U	15 U	4.4	3.0 U	36 U	7.0 U	1.9
Mercury	ND< 0.45 #	0.52 AU	15	0.75	1.5 AU	0.15 U	1.7	1.0 U	0.16 AU
Molybdenum	0.22	0.34 U	0.25 AU						
Nickel	1.9 U	0.56	6.0 U						
Selenium	0.47 U	ND< 0.08 #	39	21 U	ND< 0.08 #	1.6 U	ND< 0.07 #	ND< 0.07 #	ND< 0.061 #
Vanadium	0.31	0.35	1.0	ND< 9.8 BU	ND< 11 #	ND< 10 #	58 AU	ND< 9.1 #	ND< 8.4 #

ESP Electrostatic Precipitator
FF Fabric Filter
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Table 2-8.1 Removal Efficiencies of ESPs and Baghouses

	ESP				Baghouse			
	Inlet Conc Range	Removal Efficiencies, Percent			Inlet Conc Range	Removal Efficiencies, Percent		
		Min	Max	Mean		Min	Max	Mean
Units: $\mu g/Nm^3$								
Antimony	12-298	89.6	99.97	97.3	9-94	88.2	99.7	96.7
Arsenic	47-2274	85.2	99.9	96.8	16-3270	98.8	99.98	99.5
Barium	240-24500	92.7	99.84	98.8	241-95700	98.1	99.98	99.5
Beryllium	9-130	25.4	99.93	92.4	9-385	58.1	99.98	91.3
Boron	200-74000	19.4	98.7	62.2	35000-43200	97.6	98	97.8
Cadmium	3-166	44.0	97.3	89.7	3-726	78.7	99.995	93.2
Chromium	130-2900	94.7	100.14	97.7	64-2710	99.2	99.994	99.5
Cobalt	23-442	68.8	99.95	93.3	33-1030	85.7	99.96	97.2
Copper	11-1100	62.0	99.7	94.7	258-3710	99.3	99.96	99.7
Lead	73-1440	92.1	99.8	97.2	57-888	98.7	99.95	99.4
Manganese	140-11100	89.5	99.85	96.9	111-26100	99.0	99.93	99.5
Mercury	2-28	0	72.7	22.2	2-16	0	77.9	49.8
Molybdenum	3-1100	86.0	99.5	95.9	15-1100	97.7	99.8	99.0
Nickel	57-2100	89.2	99.9	96.5	37-16130	83.7	99.97	96.3
Selenium	0.3-408	7.6	99.8	53.9	0.2-423	17.0	99.98	80.3
Vanadium	120-4900	90.1	99.93	97.1	151-8140	98.2	100	99.5

PLANTS INCLUDED: (ESPs)

Bailly
Baldwin, Non-soot-blowing
Baldwin, Soot-blowing
Burger
Cardinal
Coal Creek
Hammond
Nelson Dewey
Niles
AirPol GSA
Smith
TIDD
Yates

PLANTS INCLUDED: (Baghouses)

Arapahoe
Boswell
Burger, SNRB
SNOX
AirPol GSA
Springerville

Table 2-8.2 Removal Efficiencies in Scrubbers

	Wet Scrubbers				Dry Scrubber/Baghouse		
	Inlet Conc	Removal Efficiencies, %			Inlet Conc	Removal Efficiencies, %	
Units: $\mu g/Nm^3$		Min*	Max	Mean		Scrubber	Overall
Antimony	0.41-43	-58	84	34	6.8	0	99.3
Arsenic	1.8-132	29	93	60	186	0	99.9
Barium	75-1920	-14	96	57	35000	0	99.95
Beryllium	1.7-99	53	93	78	112	0	> 99.96
Boron	202-17400	71	94	85	7350	0	90.5
Cadmium	1.3-163	46	90	61	264	0	99.99
Chromium	11-2080	30	77	56	935	0	99.99
Cobalt	2-191	45	85	70	380	0	> 99.9
Copper	5.6-958	70	88	77	1320	0	99.9
Lead	0.83-1440	27	97	69	140	0	99.0
Manganese	33-1200	5.1	78	49	6890	0	99.8
Mercury	4.2-12	-8.9	53	30	8.35	0	(Negative)
Molybdenum	1.4-760	50	83	62	161	0	98
Nickel	6.2-1240	-76	70	-0.8	593	0	> 99.9
Selenium	15-408	-16	67	30	118	0	> 99.96
Vanadium	5.1-2590	9.6	96	61	2920	0	99.96

PLANTS INCLUDED: Bailly, Coal Creek, Yates

* Negative removal efficiency occurs when some of the material brought in with the recycled wash is entrained in the flue gas stream.

PLANTS INCLUDED: Springerville

(Note: Spray Dryer has no solids removal. All solids are carried into baghouse.)

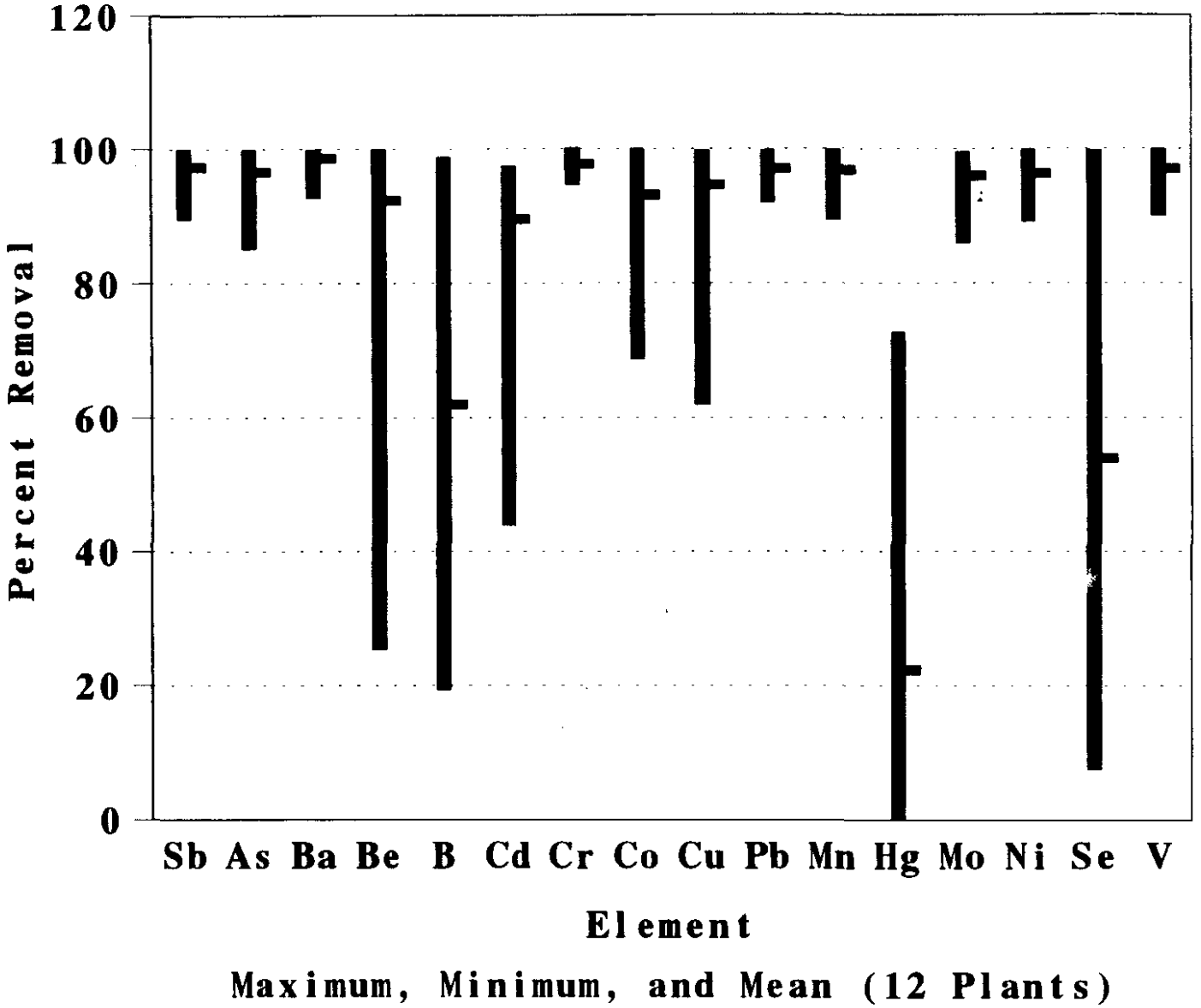

FIGURE 2-1. ESP REMOVAL EFFICIENCIES

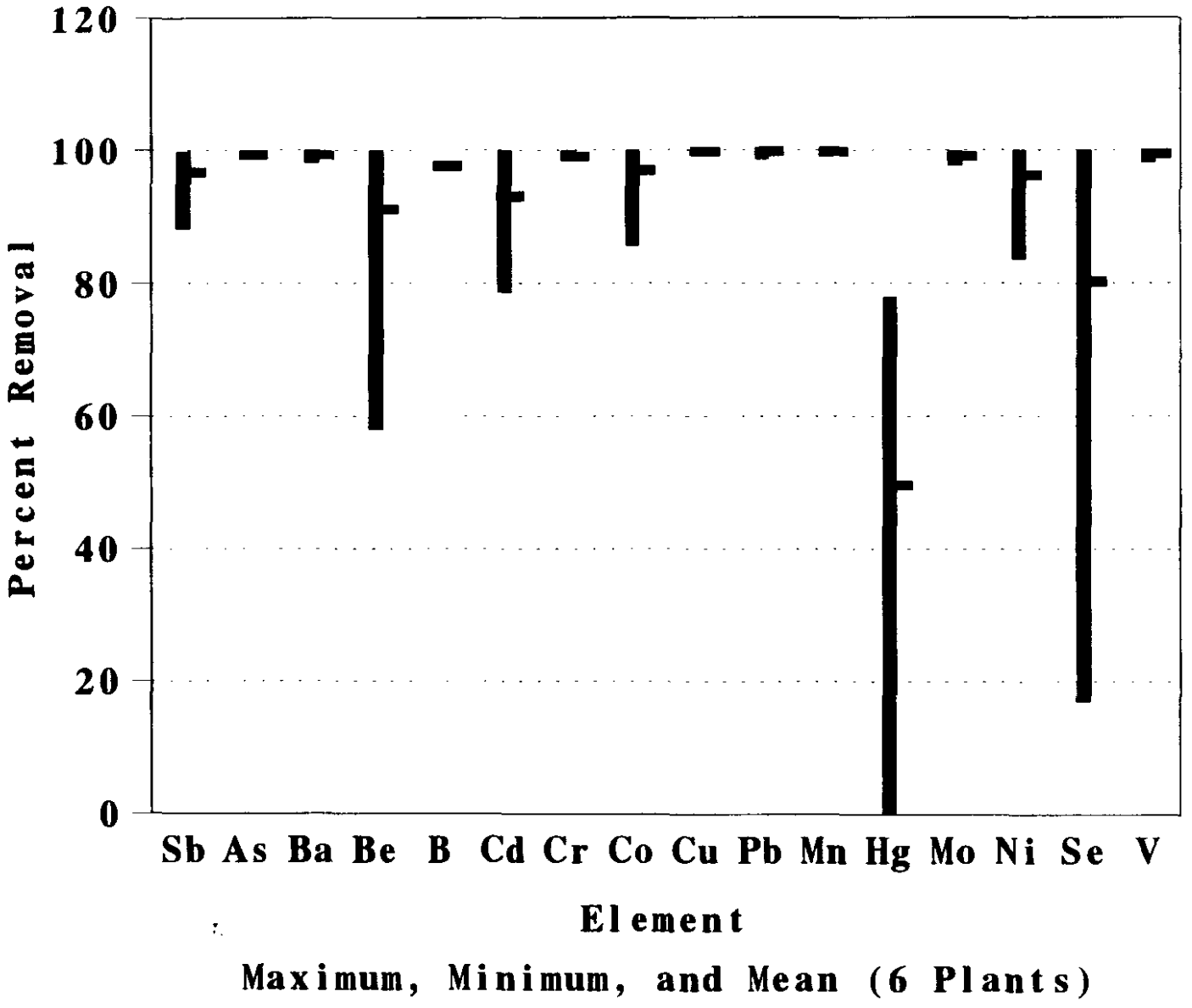

FIGURE 2-2. BAGHOUSE REMOVAL EFFICIENCIES

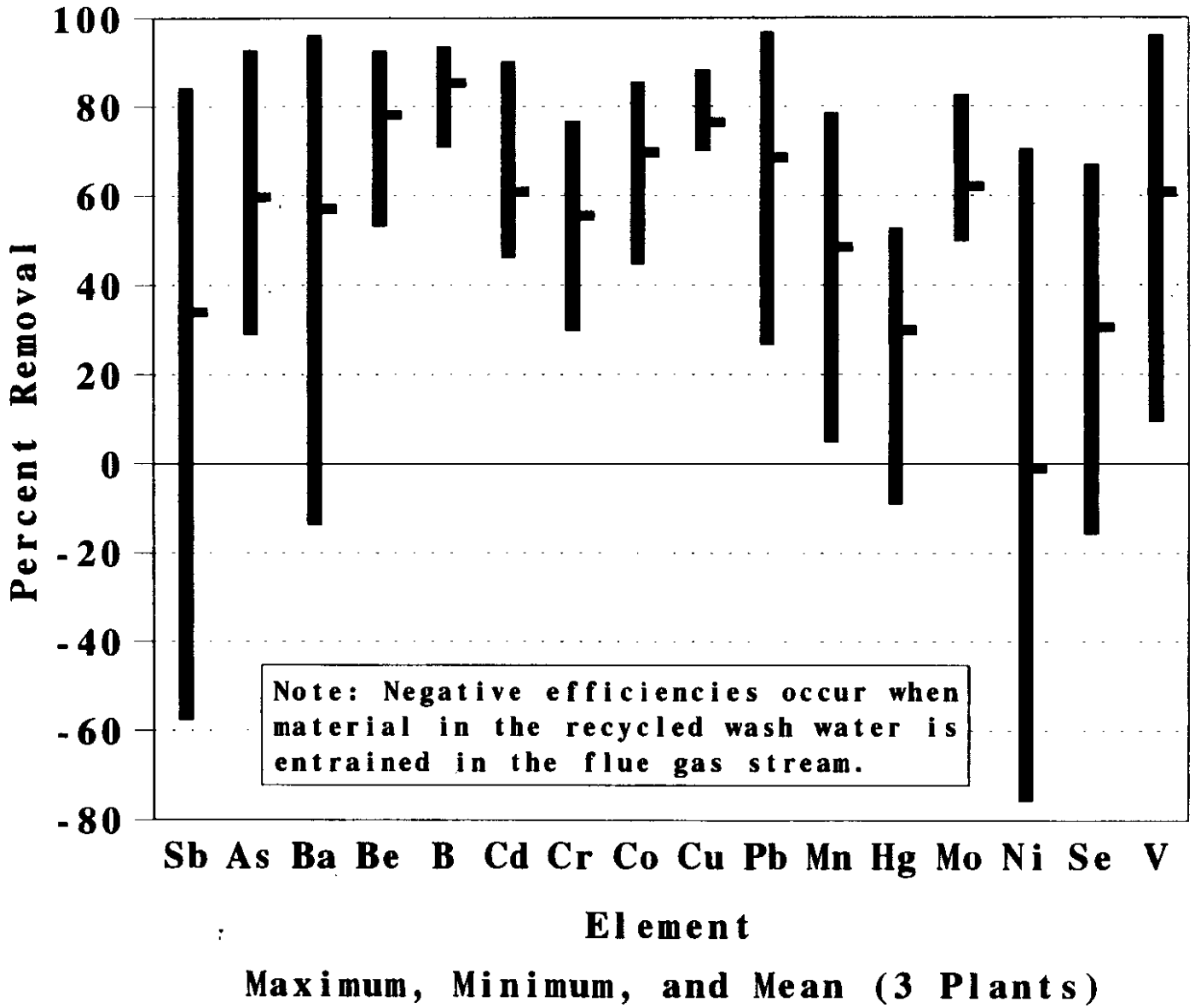

FIGURE 2-3. WET SCRUBBER EFFICIENCIES

Table 2-9 Flue Gas Sampling Methods for Hazardous Air Pollutants

Site/ Contractor	Particulate	Particle Size Distribution	Minor & Trace Elements (Including Mercury)	Halide Gasses[1] and NH_3 & HCN	Aldehydes and Ketones	Semi-Volatile Organic Compounds[2]	Volatile Organic Compounds
Baldwin/Roy F. Weston, Inc.	EPA Method 5/26A EPA Method 5/17/26A	EPA Method 201A (modified[3] by addition of a 3-Stage cyclonic separator) Malvern Particle Size Analyzer	EPA Draft Method 29 (modified by EPA Method 17) Bloom Method	EPA Method 17/26A EPA Method 5/26A HCN - Modified 26A NH_3 - Modified 26A	EPA Method SW-846 0011/0011A	EPA Method SW-846 0010/8270 EPA Method 23	EPA Method SW-846 0030/5040 (VOST)
Niles/Battelle (Columbus)	EPA Draft Method 29	Cascade Impactors	EPA Draft Method 29 HEST	EPA Method 26A HCN - APHA-808 NH_3 - APHA-401	EPA Method TO-5 EPA Method SW-846 0011 APHA 122	Modified EPA Method 23 EPA Method 23	EPA Method SW-846 0030/5040 (VOST) Summa Canister
Site 110/ Southern Research Institute	EPA Draft Method 29	Cyclonic Separation Cascade Impactors (University of Washington, Mark V)	EPA Draft Method 29 Bloom Method	Radian Corporation's Modified EPA Method 26A (includes NH_3 & HCN)	Radian Corporation's Modified EPA Method SW-846 0011	EPA Method SW-846 0010 (no analysis for Dioxins and Furans)	EPA Method SW-846 0030 (VOST)
Boswell/ Roy F. Weston, Inc.	EPA Method 5/26A EPA Method 5/17/26A	EPA Method 201A (modified by addition of a 3-stage cyclonic separator) Malvern Particle Size Analyzer	EPA Draft Method 29 (modified by EPA Method 17) Bloom Method	EPA Method 17/26A EPA Method 5/26A HCN - Modified 26A NH_3 - Modified 26A	EPA Method SW-846 0011	EPA Method SW-846 0010/8270 EPA Method 23	EPA Method SW-846- 0030/5040 (VOST)
Site 116 (SNRB)/ Radian Corporation	EPA Method 26A	(Not Performed)	EPA Draft Method 29 Bloom Method	EPA Method 26A (NH_3 & HCN not sampled)	EPA Methods SW-846 0011/TO-11	EPA Method SW-846 0010 EPA Method 23	EPA Method 18/TO-14
Nelson Dewey/ Acurex Environmental Corporation	EPA Method 5 EPA Method 17	(Not Performed)	EPA Method SW-846 0012	CARB Method 421 (NH_3 & HCN not sampled)	CARB Method 430	EPA Method SW-846 0010/8270 (no analysis for Dioxins and Furans)	EPA Method SW-846 0030 (modified w/carbon molecular sieve sorbent)
Springerville/ Southern Research Institute	EPA Method 17	EPA Method 5 with Cyclones and Cascade Impactors	EPA Draft Method 29 Bloom Method	EPA Method SW-846-0050 (modified for HCN & NH_3)	Modified EPA Method SW-846-0011 EPA Method TO-5	EPA Method SW-846 0010/8270 (and Modified 0010)	EPA Method SW-846 0030 (VOST)

Table 2-9 Flue Gas Sampling Methods for Hazardous Air Pollutants, (continued)

Site/ Contractor	Particulate	Particle Size Distribution	Minor & Trace Elements (Including Mercury)	Halide Gasses[1] and NH_3 & HCN	Aldehydes and Ketones	Semi-Volatile Organic Compounds[1]	Volatile Organic Compounds
Yates/Radian Corporation	EPA Method 5 EPA Method 17	Cascade Impactors (in-stack)	EPA Draft Method 29 Bloom Method	Radian Corporation's Modified EPA Method 26A (includes NH_3 & HCN)	Modified EPA Method SW-846-0011	EPA Method SW-846 0010 Modified EPA Method 23	EPA Method SW-846 0030 (VOST)
Coal Creek/ Battelle (Columbus)	EPA Method 5	Glass Cyclones	EPA Draft Method 29 HEST	EPA Method 26A CARB Method 421 HCN - APHA-808 NH_3 - APHA-401	APHA 122 EPA Method TO-5	Modified EPA Method 23 EPA Method 23	EPA Method SW-846 0030 (VOST) Summa Canister
SNOX/Battelle (Columbus)	EPA Method 5	Glass Cyclones	EPA Draft Method 29 HEST	EPA Method 26A CARB Method 421 HCN - APHA-808 NH_3 - APHA-401	APHA 122 EPA Method TO-5	Modified EPA Method 23 EPA Method 23	EPA Method SW-846 0030 (VOST) Summa Canister
Site 16/Radian Corporation	EPA Method 5	Cascade Impactors (University of Washington, Mark V)	EPA Draft Method 29 Bloom Method	Radian Corporation's Modified EPA Method 26A (NH_3 & HCN not sampled)	EPA Method SW-846-0011	EPA Method SW-846 0010 (no analysis for Dioxins and Furans)	EPA Method SW-846 0030 (VOST)
Cardinal/ Energy and Environmental Research Corporation	EPA Method 5	In-situ 5-stage cyclonic separation In-situ Anderson Cascade Impactors	EPA Draft Method 29 Charcoal Traps	EPA Method 26A (with modifications for NH_3 and HNC)	Modified EPA Method SW-846-0011	EPA Method SW-846 0010 EPA Method 23	EPA Method SW-846 0030 (VOST) Charcoal Tubes
Bailly/ Southern Research Institute	EPA Method 17	Cyclone Trains and Impactors	EPA Draft Method 29 Carbon Traps Bloom Method	EPA Method SW-846 0050 (with modifications for NH_3 and HNC)	Modified EPA Method SW-846 0011	EPA Method SW-846 0010/8270 (and Modified 0010)	EPA Method SW-846 0030 (VOST)
TIDD PFBC/ Radian Corporation	EPA Method 5	Cascade Impactors	EPA Draft Method 29	Radian Corporation's Modified EPA Method 26A (includes NH_3 & HCN)	EPA Method SW-846 0011/0011A	Modified EPA Method SW-846 0010 Modified EPA Method 23	EPA Method SW-846 0030/5040 (VOST)
Shawnee Unit #9/ Energy and Environmental Research Corporation	EPA Draft Method 5	(Not Performed)	EPA Draft Method 29	EPA Method 26A (NH_3 & HCN not sampled)	(Not Performed)	(Not Performed)	(Not Performed)

Table 2-9 Flue Gas Sampling Methods for Hazardous Air Pollutants, (continued)

Site/ Contractor	Particulate	Particle Size Distribution	Minor & Trace Elements (Including Mercury)	Halide Gasses[1] and NH_3 & HCN	Aldehydes and Ketones	Semi-Volatile Organic Compounds[2]	Volatile Organic Compounds
Arapahoe Unit #4/ Public Service Company of Colorado	EPA Method 5	(Not Performed)	EPA Draft Method 29 Bloom Method	CARB Method 421 HCN - CARB-426 NH_3 - Modified EPA-26A	CARB Method 430	CARB Method 429 EPA Method 23	CARB Method 422(Tedlar Bags)/TO-14

FOOTNOTES

1. *The presence of halogen gasses (X_2) in coal flue gas is controversial as is their determination by EPA Method 26A.*
2. *Analyses for dioxins and furans were preformed except where otherwise indicated.*
3. *Only major modifications such as structural changes to sampling trains, for example the addition of cyclonic separators, and procedural changes such as an extraction step that might distinguish the analytes specific to, for example, the very similar EPA Method SW-846 0010 and EPA Method 23 will be noted as modifications to the standard procedures.*

ACRONYMS and TERMINOLOGY

APHA	*American Public Health Association Method.*
Bloom Method	*Mercury chemical speciation method developed by Nicholas Bloom and workers.*
CARB	*California Air Resources Board.*
EPA	*U. S. Environmental Protection Agency.*
HEST	*Hazardous Emissions Sampling Train, developed by John Cooper and workers.*

SECTION 3.0 INDIVIDUAL SITE RESULTS

This section contains selected results from each plant site. The data given here are reported in the units used in the individual reports except where calculations were necessary. Units may differ slightly. For example, gas stream concentrations for all plant sites are reported in micro-grams/normal cubic meter (μg/Ncm). Some contractors, however, reported results on a dry basis (μg/dscm, micro-grams/dry standard cubic meter), and some did not. Some concentrations were corrected to 3 percent oxygen, and some were not.

The stream numbers on the plant schematics correspond to the column numbers in the tables of stream flow rates.

Section 3.1 Coal Creek Station

The Coal Creek Station is located about 50 miles north of Bismarck, North Dakota, near Underwood, North Dakota. Coal Creek Station is a two-unit, zero discharge, 1,100 MWe, mine-mouth plant located in a lignite field. The two units are identical. The study described in this report was conducted on Unit No. 1. Each unit has a tangentially fired, water walled, dry bottom furnace, with a Combustion Engineering Controlled Circulation boiler. The furnace is fueled by lignite that is conveyed into the plant from the Falkirk mine located adjacent to the plant. Coal is fed to the boiler through eight pulverizers, of which seven are in operation at any one time. Each unit is equipped with an electrostatic precipitator (ESP) for particulate removal, and with a wet flue gas desulfurization unit (FGD, denoted as scrubber) for sulfur dioxide (SO_2) removal. Each of these components is described below.

Lignite is supplied to the plant from the nearby Falkirk mine by a conveyer system over 3 miles long. A series of conveyers and silos allows for supply of the plant, and for movement of coal in and out of yard storage supplies. The lignite is crushed, prior to being supplied to eight silos in each unit of the plant. The crushed lignite from the silos is then pulverized in eight bowl mills, which grind the coal to a fineness of 65 percent through 200 mesh. Only seven of the eight mills are in operation at any time. The pulverizing process also reduces the moisture content of the coal by about half. The pulverized lignite is transported to the furnace pneumatically, and injected into the furnace through tangential nozzles at eight levels in the windbox registers in the front and rear furnace walls.

Coal Creek Unit 1 is designed to achieve low NO_x production by means of the tangential firing, which produces a vortex in the furnace, causing mixing of the fuel and air streams throughout the furnace. Internal recirculation of gas within the furnace vortex

provides low NO_x production, and results in a long residence time for combustion, favoring low hydrocarbon and CO emissions. Reduction of NO_x is also achieved by addition of overfire air.

Soot blowing at Unit 1 is conducted continuously on at least some portion of the furnace, using a total of 262 steam soot blowers installed in the furnace.

The flue gas leaving the Unit 1 boiler travels through an economizer and then through two parallel air preheaters (not shown) on its way to the two parallel halves of the ESP. The two halves of the ESP are shown as ESP #1 and ESP #2 in Figure 3.1-1. Gas leaving the preheaters is divided into four ducts, two of which connect to each half of the ESP. The ESP is constructed as two separate shells or halves, permitting operation with one shell under reduced load conditions.

The ESP provides a specific collecting area of 599 square feet per 1000 actual cubic feet per minute of gas flow. ESP is rated at a removal efficiency of 99.5 percent at inlet particulate loadings of greater than 1.16 grains per actual cubic foot (2.65 grams per actual cubic meter). At lower inlet loadings, the outlet particulate loading is rated to be no higher than 0.0058 grains per actual cubic foot (0.013 grams per actual cubic meter).

Ash from the hoppers is removed by a pressurized pneumatic system that dumps two hoppers at a time. Flue gas leaves the ESP in four ducts which connect to four induced draft fans. The gas flow from these fans recombines into two ducts that connect to the Unit 1 scrubber system.

The Coal Creek Unit 1 scrubber is a Combustion Engineering Air Quality Control System (AQCS), which removes SO_2 from the flue gas by means of four countercurrent spray towers using an alkali slurry. The system is designed to remove 90 percent of the SO_2

from up to 60 percent of the flue gas flow. The unscrubbed (by-passed) flue gas is recombined with the scrubbed gas to reheat it. Flexibility in responding to variations in fuel sulfur content is provided by the variable gas bypass flow, and by the capability of operating with fewer than four spray towers at a time.

In the scrubber, alkaline slurry is pumped to the spray towers from two slurry reaction tanks (not shown), and drains back after collection at the bottom of the scrubber. The scrubber slurry is maintained at a pH of about 7 by intermittent automatic introduction of lime slurry into the reaction tanks. The lime slurry is made up as needed from commercial pebble lime and scrubber makeup water, to a nominal solids content of 15 percent. This slurry is added to the reaction tanks, along with scrubber makeup water for tank level control. Scrubber makeup water also enters the system as an intermittent flow of mist eliminator wash water (not shown).

The scrubber bypass flow can be adjusted by means of dampers in the flow line. The bypass flow results from the convergence (from opposite directions) of the two combined flow streams downstream of the four induced draft fans at the outlet of the ESP. At the convergence point, the combined bypass flows turn vertically to meet the scrubbed flue gas flow exiting the scrubber. As a result of the contorted bypass flow path, the gas velocity profile in the bypass duct is highly non-uniform.

During the six days of measurement in this study, the scrubber was operated in a normal manner. As a result, scrubber operation varied in response to variations in the sulfur content of the feed coal. Because of this factor, all four of the scrubber spray towers were in service on the first, fifth, and sixth days of measurements, but only three were in service on the second, third, and fourth days. Changeover between the two modes of operation was done after the completion of flue gas measurements on each day.

A schematic flow diagram is shown in Figure 3.1-1 and Figure 3.1-2 shows the partitioning results for the trace elements. Tables 3.1-1 and 3.1-2 present the trace element flow rates and concentration/removal efficiency information for this plant. Table 3.1-3 gives the stream temperatures at various points in the plant.

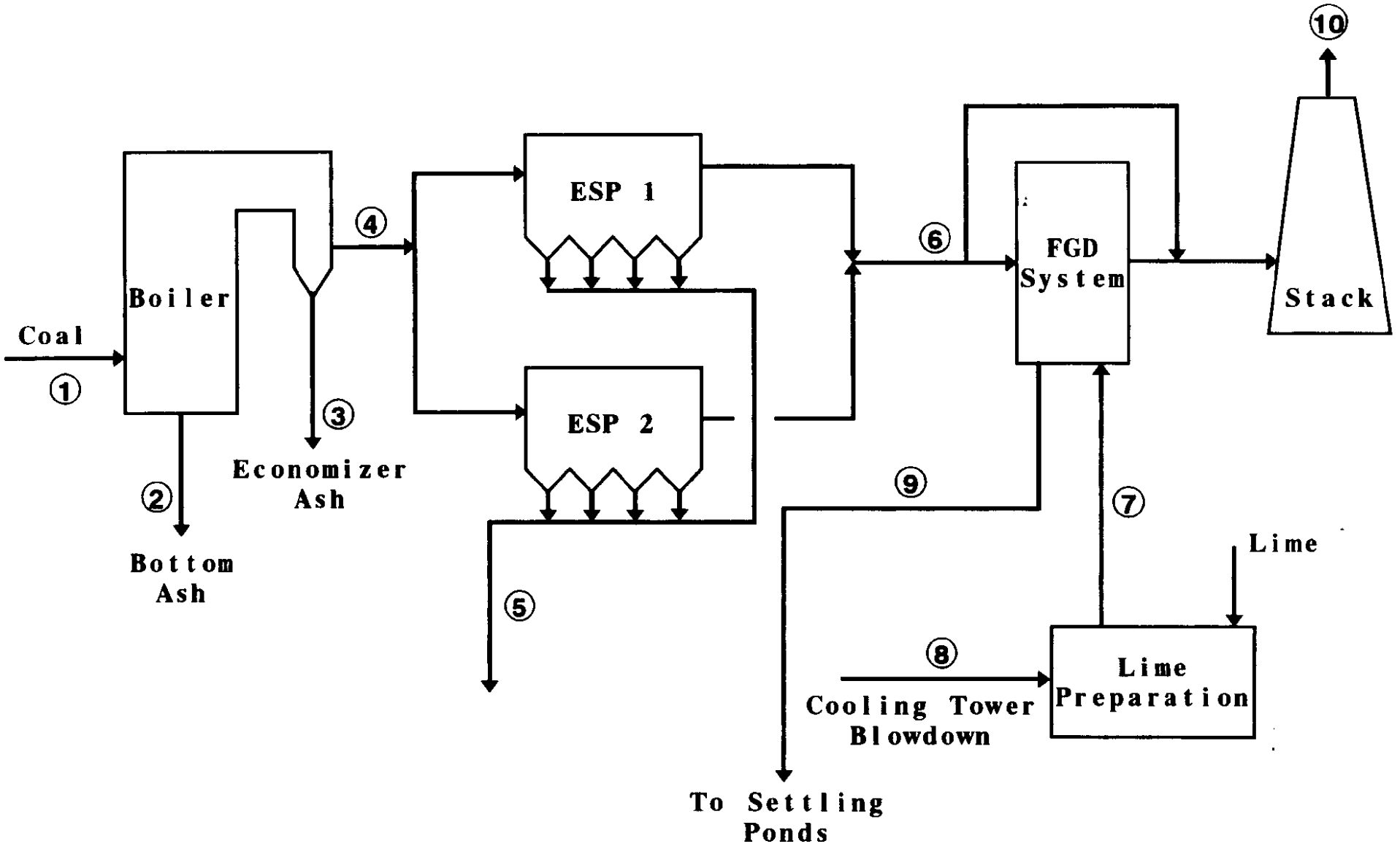

FIGURE 3.1-1. COAL CREEK STATION UNIT NO.1 FLOW DIAGRAM

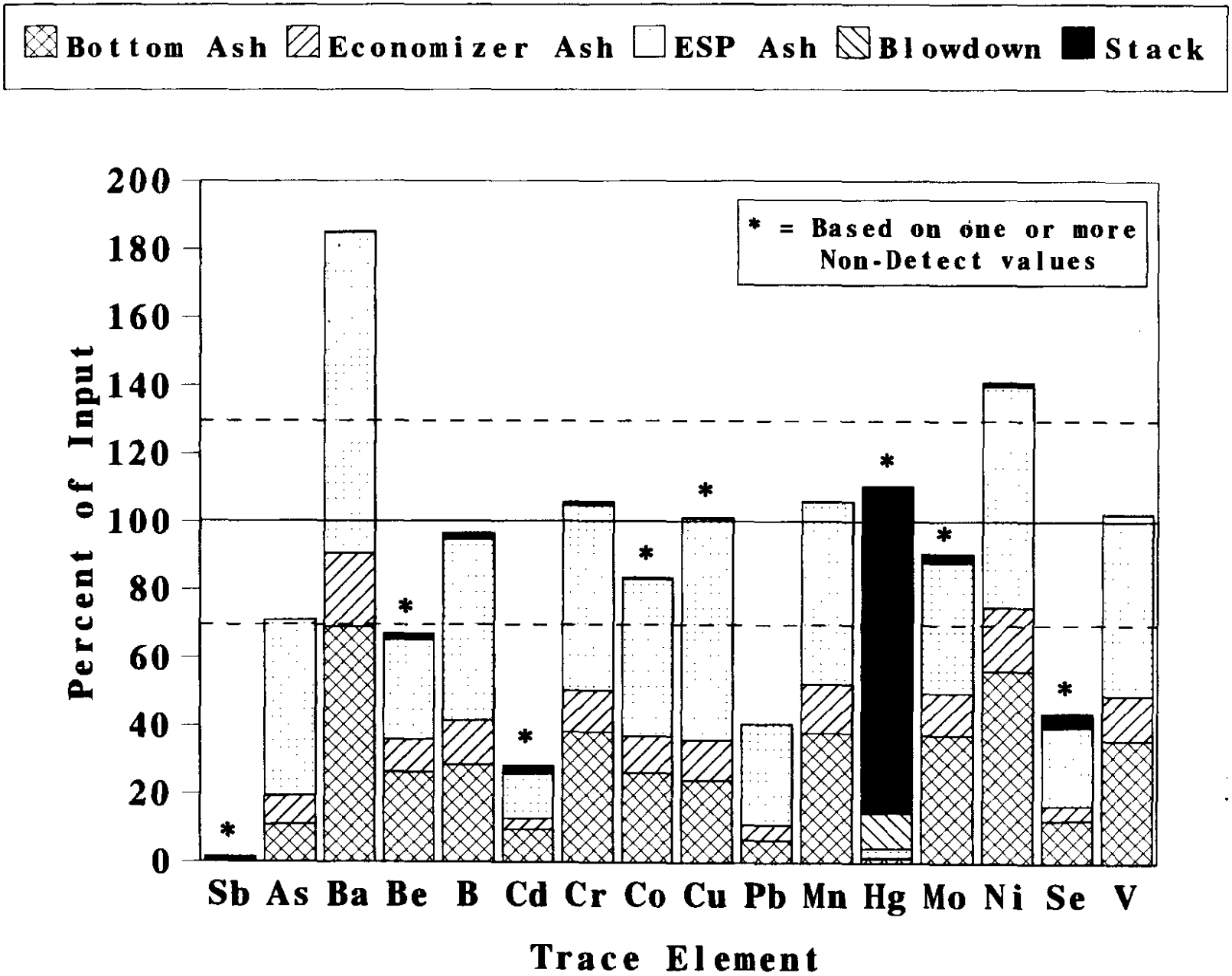

FIGURE 3.1-2 TRACE ELEMENTS IN OUTPUT STREAMS COAL CREEK STATION

Table 3.1-1 Trace Element Flow Rates, Coal Creek Station

	(1) Coal	(2) Bottom Ash	(3) Economizer Ash	(4) ESP Inlet	(5) ESP Catch	(6) ESP Out, Scrubber In	(7) Lime Reagent	(8) Recycle/ Makeup Water	(9) Srubber Blowdown	(10) Stack
Units: lb/hr										
Antimony	ND< 24.8 #	ND< 0.136 #	ND< 0.0451 #	0.310	0.185[C]	0.0062	ND< 0.208 #	ND< 0.0059 #	ND< 0.0025 #	0.0010
Arsenic	6.30	0.712	0.541	4.64	3.37	0.010	ND< 0.208 #	ND< 0.0059 #	0.0110	0.0069
Barium	218	152	47.4	90.3	207	1.07	1.25	0.0439	0.265	0.876
Beryllium	0.449	0.146	0.053	0.170	0.163	ND< 0.012 #	ND< 0.104 #	ND< 0.0015 #	ND< 0.0006 #	ND< 0.0093 #
Boron	95.8	28.0	12.9	57.5	52.4	0.97	ND< 2.61 #	3.22	1.39	0.105
Cadmium	ND< 0.603 #	ND< 0.0678 #	ND< 0.0226 #	0.0737	ND< 0.0924 #	ND< 0.021 #	0.104[B]	0.0015[A]	0.0006[B]	ND< 0.0174 #
Chromium	5.49	2.14	0.688	3.83	3.05	0.048 [A]	0.104[B]	0.0044	0.0101	0.0525
Cobalt	1.47	0.441	0.180	0.969	0.779	ND< 0.012 #	ND< 0.208 #	ND< 0.0029 #	0.0013[A]	ND< 0.0089[B]
Copper	4.69	1.15	0.564	2.50	3.13	0.0315	ND< 0.104 #	ND< 0.0015 #	0.0067	ND< 0.0109[A]
Lead	4.89	0.339	0.226	1.52	1.51	0.0044	ND< 0.208 #	ND< 0.0059 #	0.0025[A]	0.0037
Manganese	65.0	28.9	11.0	40.9	40.7	0.163	11.1	0.0322	0.480	0.161
Mercury	0.0536	ND< 0.0007 #	0.0002[B]	0.0516	0.0014	0.0811	ND< 0.0010 #	ND< 0.00006 #	0.0058	0.0525
Molybdenum	1.54	ND< 1.36 #	0.451[B]	0.829	ND< 1.39 #	0.0068	ND< 2.08 #	0.173	0.0783	0.0027
Nickel	1.74	1.19	0.395[A]	2.48	1.37	0.0274[B]	0.365[A]	ND< 0.0029 #	0.0139	0.0278
Selenium	ND< 0.871 #	ND< 0.136 #	ND< 0.0451 #	0.413	0.249[A]	0.087	ND< 0.209 #	0.0059[B]	ND< 0.0025 #	0.0444
Vanadium	10.1	3.73	1.38	4.05	5.53	0.0287	0.3336	0.0129	0.0189	0.0238

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples

Table 3.1-2 Concentrations and Collection Device Removal Efficiencies, Coal Creek Station

	ESP In, $\mu g/Nm^3$	Scrubber In, $\mu g/Nm^3$	Stack $\mu g/Nm^3$	ESP Removal Efficiency, Percent	Scrubber Removal Efficiency, Percent
Antimony	69.8	1.65	0.25	97.2	76.1
Arsenic	1,046	2.12	1.7	99.8	29.1
Barium	20,348	205	217	98.8	-13.6
Beryllium	38.2	2.35	ND< 2.3	96.5	> 53.3
Boron	12,956	237	26	98.3	71.0
Cadmium	16.6	4.11	ND< 4.3	81.4	> 46.2
Chromium	864	12.9	13	98.5	29.9
Cobalt	218	2.35	ND< 2.2	99.4	> 44.7
Copper	563	6.58	ND< 2.7	98.8	> 71.4
Lead	342	0.976	0.92	99.7	26.7
Manganese	9,219	38.8	40	99.6	5.1
Mercury	11.6	14.1	13	-64.9	-8.9
Molybdenum	187	1.65	0.68	99.1	54.1
Nickel	558	7.29	6.9	98.8	2.7
Selenium	93.0	17.6	11	79.2	39.7
Vanadium	914	6.00	5.9	99.3	9.6

Table 3.1-3 Stream Temperatures, Coal Creek Station

Temperature, deg F	
Steam, Superheater Outlet	1004
Steam, Reheater Outlet	1005
ESP Inlet	340
ESP Outlet, Scrubber Inlet	317
Scrubber Outlet (To Stack)	230

Section 3.2 Boswell Energy Center

Plant Description

The Boswell Energy Center is located in Cohasset, Minnesota, and is owned and operated by Minnesota Power Company. The power plant comprises four coal-fired units numbered 1 through 4. Units 1 and 2 are each rated at 69 MWe, Unit 3 is rated at 350 MWe, and Unit 4 is rated at 500 MWe. Unit 2, built in 1957, was studied in this program. This unit, equipped with a Riley Stoker front-fired boiler, burns western subbituminous coal delivered to the station by train from the Powder River Basin area of Montana and Wyoming, primarily from the Rosebud seam. Average coal characteristics for this study were 8.4% ash, 0.70% sulfur, 24.8% moisture, and approximately 8,800 Btu/lb higher heating value.

Unit 2 is operated from a control room which is common to both Units 1 and 2. At Unit 2, coal is transferred from storage bunkers through feeders directly into four pulverizers located on the ground floor. Pulverized coal is transported via primary air through 9 burners on the front of the furnace. Secondary combustion air is introduced to the furnace through a windbox. The combustion gases leave the furnace and enter the convective pass section of the boiler which is composed of vertically divided superheater and reheater sections. Main and reheat steam temperatures are controlled primarily by dampers at the outlets of the superheater and reheater sections, and/or by a superheater/reheater bypass duct. Superheater and reheater attemperation sprays are available, but seldom used.

Next, the combustion gases are directed through an economizer section followed by an air preheater section. Some entrained particulate (i.e., ash) is deposited on various boiler wall and tube surfaces. Unit 2 is equipped with a series of sootblowers to remove this slagging and fouling material. The sootblowers are

used on an irregular basis. That is, when heat transfer patterns change, the sootblowers are used to clean the contaminated surfaces and regain optimum steam temperature control and thermal efficiency. Selected sootblowing sequences are normally executed at least once per shift, but not necessarily at the same time during each shift.

At this unit, the economizer hoppers are maintained full, resulting in the carryover of overhead ash (i.e., fly ash) to downstream collection equipment.

Unit 2 uses a baghouse for particulate control. The original mechanical particulate collector has been removed, although the housing remains as part of the ductwork leading to the retrofitted baghouse. The baghouse consists of eight compartments containing a total of 1,920 Teflon-coated fiberglass bags (240 bags per compartment), has an air-to-cloth ratio of 1.974:1, and uses reverse air for cleaning. It is designed for 99.7% particulate collection efficiency. The flue gas exit temperature is 300-400°F under normal operating conditions. Boswell Unit 2 has no other air pollution control equipment currently installed.

Flue gas is discharged from Units 1, 2, and 3 via a common stack. Maintenance is effected by directing gas flow from the common stack to an adjacent 250-foot stack using dampers in the breaching of each unit. The 250-foot stack originally served Units 1 and 2 prior to the construction of Unit 3. Since there are no provisions for emission measurement on the 250-foot stack, a suitably configured and equipped section of ductwork located downstream of the Unit 2 baghouse and upstream of an induced draft (ID) fan was selected for flue gas discharge characterization.

All overhead ash collected in the baghouse hoppers is removed from the plant site via truck.

Furnace bottom ash is sluiced to a common bottom ash pond for Units 1, 2, 3 and 4. Supernatant from the pond is used as return water for all four units, and a portion of it is blown down. The blowdown is a part of the combined supernatant from the pond; it is not specific to each unit.

A process flow diagram of Boswell Unit 2 is shown in Figure 3.2-1. Partitioning results for trace elements are presented in Figure 3.2-2. Tables 3.2-1 and 3.2-2 give the trace element flow rates and concentration/removal efficiency information for the Boswell Plant. Table 3.2-3 gives the stream temperatures at various points in the plant.

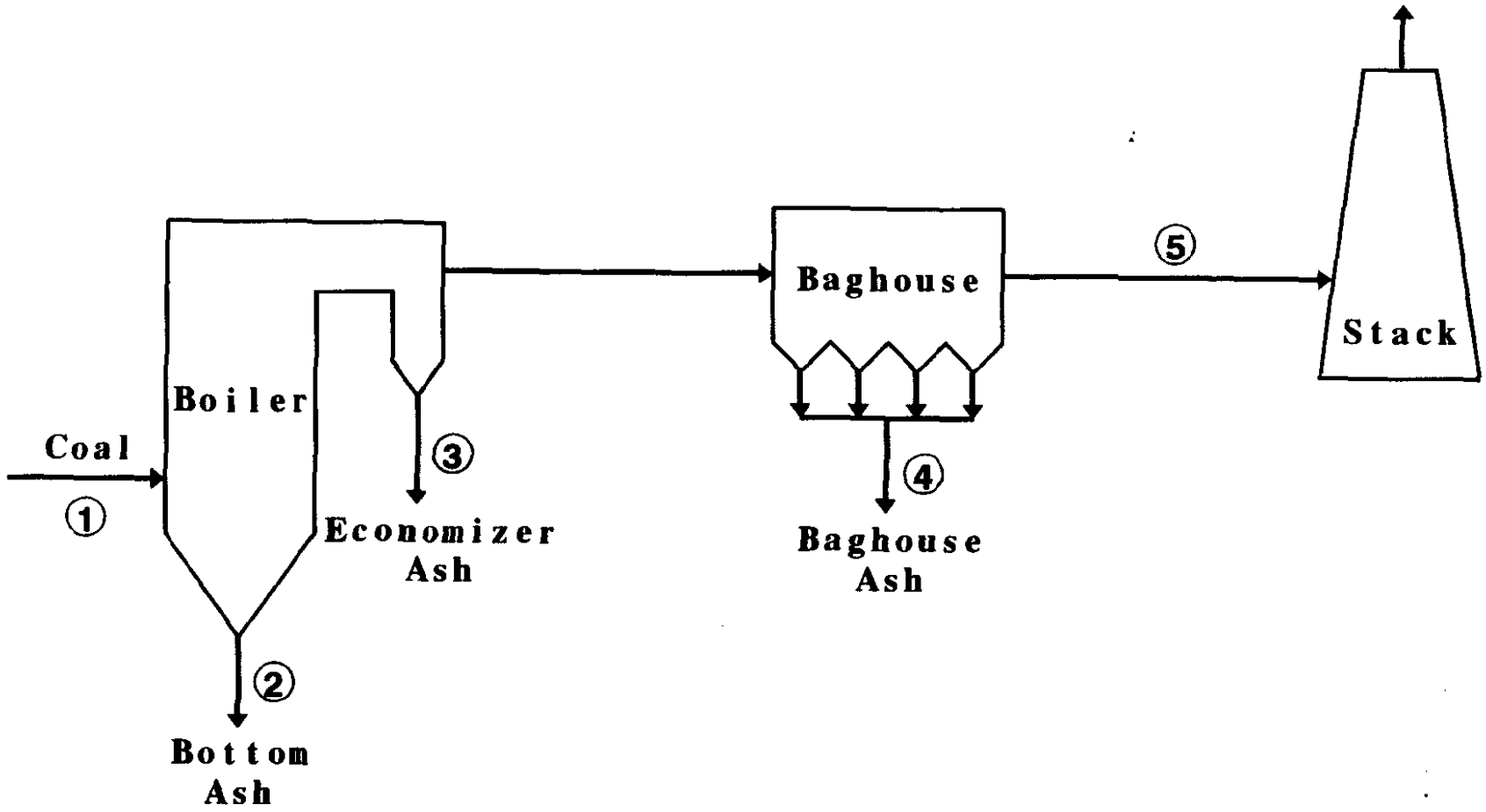

FIGURE 3.2-1. BOSWELL ENERGY CENTER UNIT NO. 2 FLOW DIAGRAM

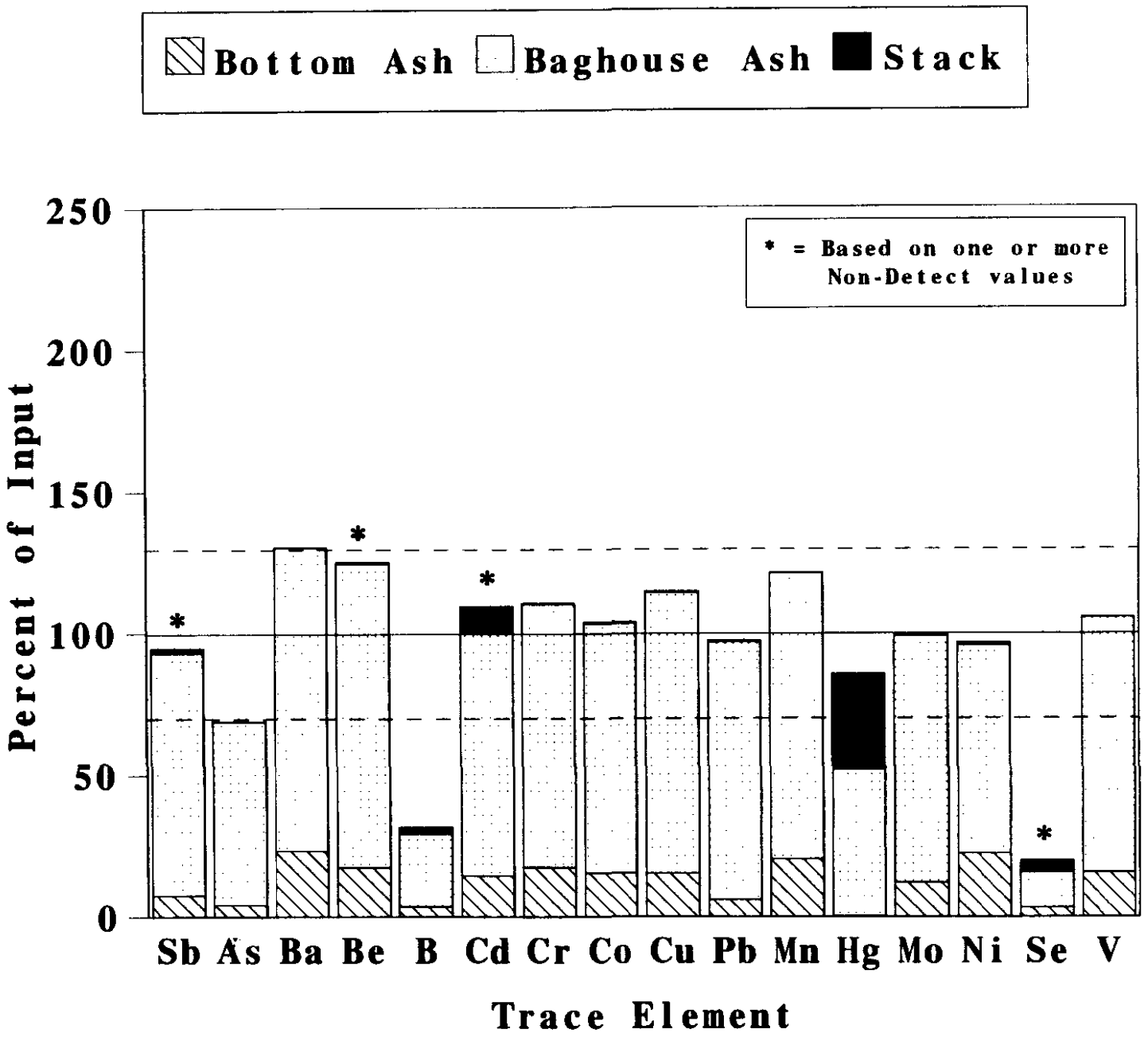

FIGURE 3.2-2. TRACE ELEMENTS IN OUTPUT STREAMS BOSWELL ENERGY CENTER

Table 3.2-1 Trace Element Flow Rates, Boswell Energy Center

	(1) Coal Input	(2) Bottom Ash	(3) Baghouse Inlet	(4) Baghouse Ash	(5) Stack
Units: lb/hr					
Antimony	0.028	0.002	0.016	0.024	ND< 0.00044 #
Arsenic	0.10	0.004	0.024	0.06	0.00021[B]
Barium	23.3	5.4	2.8	25.0	0.053
Beryllium	0.013	0.002	0.0078	0.014	ND< 0.000084 #
Boron	16.7	0.60	17	4.3	0.39
Cadmium	0.004	ND< 0.0006 #	0.0074	0.004	ND< 0.00042 #
Chromium	0.2	0.04	0.28	0.21	0.0013
Cobalt	0.07	0.012	0.07	0.066	0.00045
Copper	0.38	0.06	0.4	0.38	0.0016
Lead	0.29	0.018	0.12	0.26	0.0016[A]
Manganese	7.5	1.5	4.3	7.59	0.012
Mercury	0.004	0.000012[A]	0.003	0.0020	0.0013
Molybdenum	0.30	0.037	0.56	0.26	0.00084
Nickel	0.16	0.03	0.17	0.11	0.0013
Selenium	0.05	ND< 0.002 #	0.0061	0.006	0.0021
Vanadium	0.5	0.07	0.43	0.42	0.001

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.2-2 Concentrations and Collection Device Removal Efficiencies, Boswell Energy Center

	Baghouse Inlet, $\mu g/Nm^3$	Baghouse Outlet, $\mu g/Nm^3$	Removal Efficiency, Percent
Antimony	32	ND< 0.91	> 97.2
Arsenic	47	ND< 0.44	> 99.1
Barium	5,400	110	98.1
Beryllium	16	ND< 0.17	> 98.9
Boron	35,000	800	97.6
Cadmium	15	ND< 0.86	> 94.3
Chromium	610	2.7	99.5
Cobalt	150	0.93	99.3
Copper	850	3.2	99.6
Lead	240	3.2	98.7
Manganese	8,600	25	99.7
Mercury	6.4	2.6	59.8
Molybdenum	1,100	1.7	99.8
Nickel	360	2.6	99.2
Selenium	14	4.3	65.6
Vanadium	900	2.0	99.8

Table 3.2-3 Stream Temperatures, Boswell Energy Center

Temperature, deg F	
Baghouse Inlet	350
Baghouse Outlet (To Stack)	332

Section 3.3 Springerville Station

Springerville Generating Station Unit No. 2 is owned and operated by the Tucson Electric Power Company (TEP) and is located near Springerville, Arizona. The plant is a zero-discharge design, burning subbituminous coal from the Lee Ranch Mine in New Mexico. The coal has an average sulfur content of 0.7% and an ash content of 19%. Typical gross electrical generation at full load is 397 MWe, and the net generating capacity is approximately 360 MWe. (During testing, Unit No. 2 was operated at maximum capacity, with 422 MWe gross and 383 MWe net electrical output.)

The Unit No. 2 boiler is a corner-fired, balanced-draft design with overfire air for reducing NO_x emissions. Coal is fed to the boiler through bowl mill pulverizers. Pyrite is separated from the coal in the pulverizers. At full load, five or six pulverizers feed about 200 tons per hour of coal into 24 burners and produce 2.6 million pounds per hour of steam. Approximately 22% of the coal ash is retained as bottom ash in the boiler. The bottom ash is removed by a sluice. Soot blowers for the boiler walls are operated on a continuous cycle, and the air heater soot blowers are operated once per shift (twice daily). Pulverizer reject (pyrite) and bottom and economizer ash (sluice) are pumped to dewatering bins, surface water is passed through screens in the bins, and returned back for sluicing operations. The dewatered solids are trucked to the ash disposal area.

Unit No. 2 uses one cooling tower with 13 cells and one dual-pressure, single-shell condenser. The condensate is treated and recirculated. All makeup water for the unit is obtained from a storage pond supplied by seven nearby wells, or other waste water streams of the unit. Waste water is also treated on site and either sent to evaporation ponds or used as makeup water for other unit processes.

Unit No. 2 uses a Dry Flue Gas Desulfurization (FGD) system. The system has three spray dryer absorber (SDA) modules and one atomizer per absorber. A small portion of the flue gas (about 15% at full load) bypasses the SDA modules. Under normal conditions, at operation above 60% capacity, all three SDA modules are in service. Fresh lime from Chemstar Lime of Nelson, AZ, is slaked in ball mills at the plant. The fresh lime milk has a lag time of one to two hours from the lime milk storage tank to the injection through the atomizers. Solids content for the fresh lime slurry is maintained at 24%. The FGD system uses sorbent/ash recycle from the baghouse to supplement the fresh lime slurry. Recycle feed rate is adjusted to control the temperature of the flue gases leaving the SDA modules to 71 C (160°F). Solids content of the slurry feed at the atomizers is kept at about 50%. Air is entrained into the bottoms of the SDA modules to limit solids dropout in the modules. All of the fly ash and slurry residue pass through the SDA absorbers into the baghouse inlet ducts.

The baghouse system consists of two baghouses with 14 compartments each that withdraw flue gas from a common manifold. Filtered flue gases are pulled from the two baghouses into separate induced draft fans before being exhausted through the 152.4-m tall stack that is exclusive to Unit No. 2. Fly ash/sorbent is either recycled to the mix tank to be used in the FGD system or transported to a fly ash silo and then trucked to an ash disposal area.

Figure 3.3-1 is a schematic process flow diagram for Unit No. 2 and partitioning results for trace elements are presented in Figure 3.3-2. Tables 3.3-1 and 3.3-2 give the trace element flow rates and concentration/removal efficiency information for the Springerville Station. Table 3.3-3 gives the stream temperatures at various points in the plant.

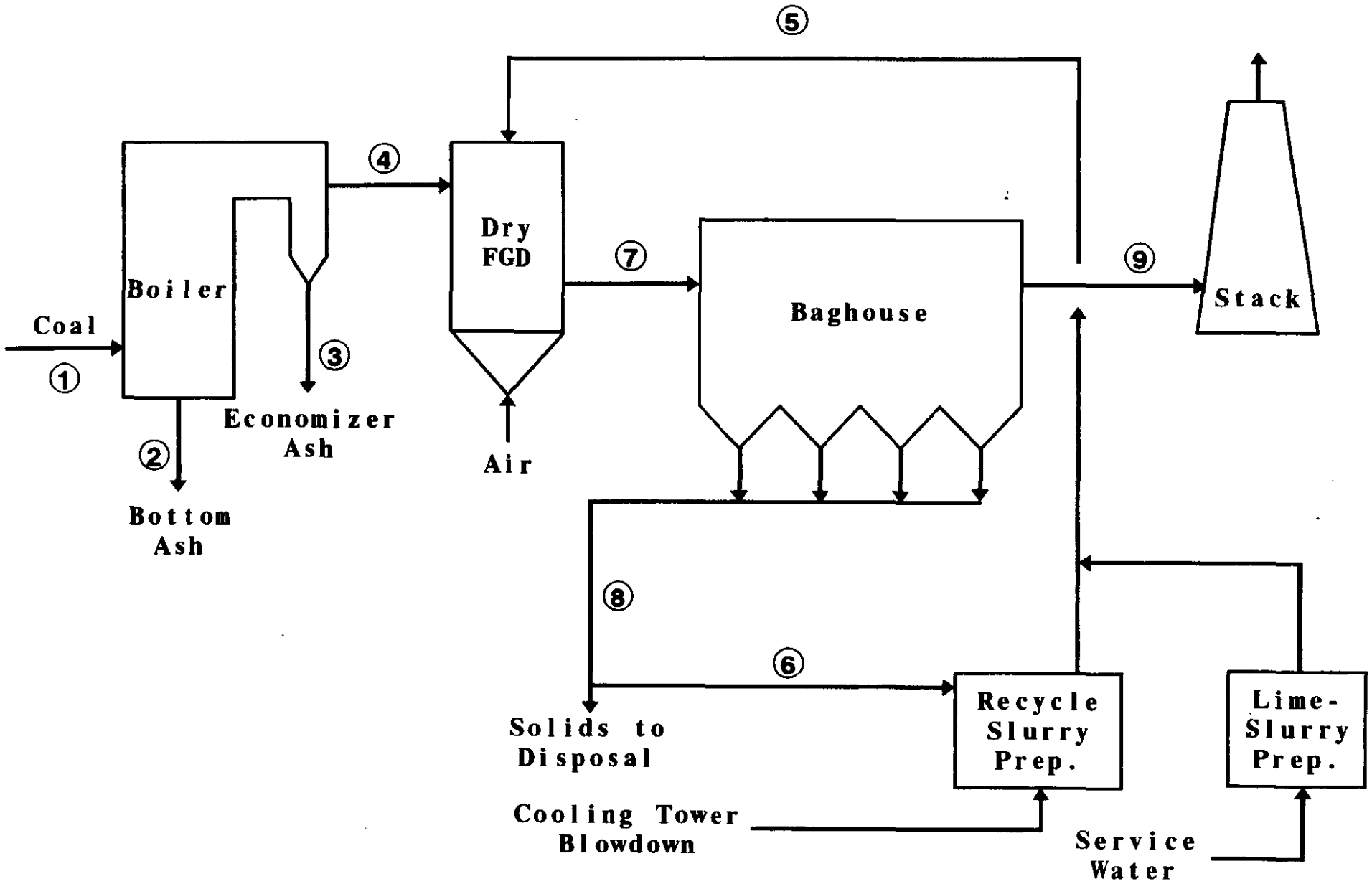

FIGURE 3.3-1. SPRINGERVILLE GENERATING STATION UNIT NO. 2 FLOW DIAGRAM

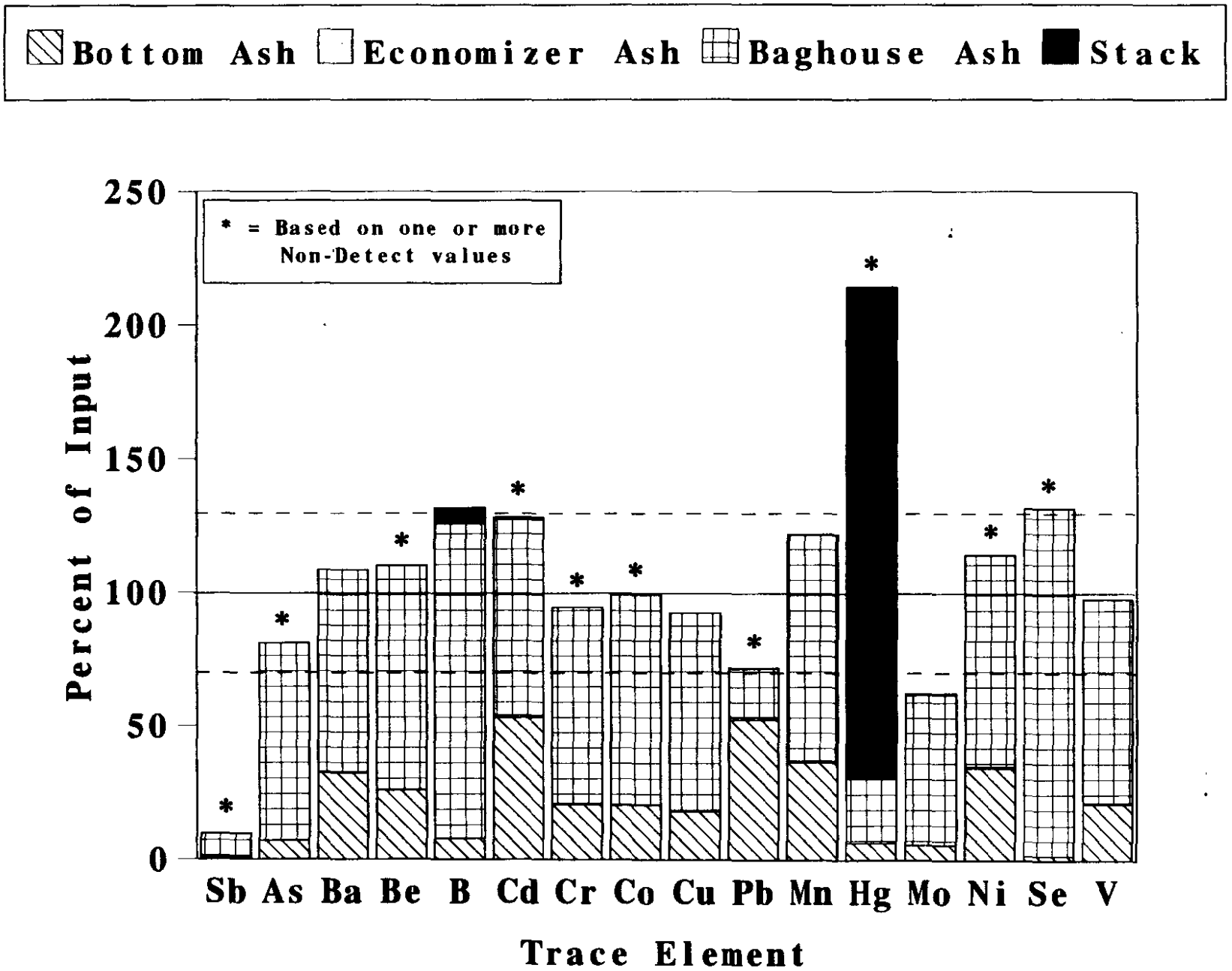

FIGURE 3.3-2. TRACE ELEMENTS IN OUTPUT STREAMS SPRINGERVILLE STATION

Table 3.3-1 Trace Element Flow Rates, Springerville Station

	(1) Coal	(2) Bottom Ash	(3) Economizer Ash	(4) Spray Dryer Inlet	(5) Lime Input	(6) Baghouse Recycle	(7) Baghouse Inlet	(8) Baghouse Ash	(9) Stack
Units: lb/hr									
Antimony	0.592	ND< 0.00586 #	ND< 0.000059 #	0.0190	ND< 0.000435 #	0.0726[B]	0.0509	0.125[B]	0.000161[A]
Arsenic	1.13	0.0783	0.00266	0.350	0.0256	1.33	2.47	2.18	ND< 0.000569 #
Barium	125.	40.5	0.433	95.2	0.0618	147.	267.	242.	0.0549
Beryllium	0.437	0.113	0.00128	0.406	ND< 0.00173 #	0.567	1.07	0.937	ND< 0.000137 #
Boron	39.1	3.07	0.0568	20.6	0.803	72.1	121.	119.	2.37[A]
Cadmium	ND< 0.0976 #	0.0518	0.000913	0.738	0.00292	0.115	2.02	0.190	ND< 0.00079 #
Chromium	3.60	0.740	0.0157	2.60	0.0562	4.14	7.55	6.84	ND< 0.000409 #
Cobalt	1.37	0.280	0.00340	1.06	0.00347	1.67	2.87	2.75	ND< 0.000546 #
Copper	4.91	0.889	0.0107	3.67	0.0493	5.67	10.4	9.37	0.00393
Lead	ND< 0.976 #	0.511	0.00944	0.390	0.00902	ND< 0.286 #	0.857	ND< 0.472 #	0.00281
Manganese	31.6	11.5	0.160	24.1	0.599	42.5	72.8	69.8	0.0708
Mercury	0.0143	0.000913	0.000001[A]	0.0233	ND< 0.000018 #	0.00533	0.0449	0.00881	ND< 0.0263 #
Molybdenum	0.857	0.0484	0.000575	0.448	0.0034	0.738	1.32	1.22	0.00556
Nickel	2.24	0.769	0.01	1.65	0.0321	2.79	4.55	4.60	ND< 0.000546 #
Selenium	0.338[A]	ND< 0.00587 #	ND< 0.000059 #	0.329	ND< 0.000435 #	0.687	1.18	1.13	0.00029[A]
Vanadium	10.4	2.20	0.0260	8.10	0.0927	12.4	22.7	20.4	0.00418

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
\# Non-detectible in all samples

Table 3.3-2 Concentrations and Removal Efficiencies, Springerville Station

	SDA Inlet, $\mu g/Nm^3$	SDA Out Baghouse Inlet, $\mu g/Nm^3$	Baghouse Outlet, $\mu g/Nm^3$	Baghouse Removal Efficiencies, Percent	Overall Removal Efficiencies, Percent
Antimony	6.8	18.2	0.058	99.7	99.3
Arsenic	186	885	0.21	99.97	99.9
Barium	35,000	95,700	20	99.98	99.95
Beryllium	112	385	ND< 0.05	> 99.98	> 99.96
Boron	7,350	43,200	865	98	90.5
Cadmium	264	726	0.037	99.995	99.99
Chromium	935	2,710	0.15	99.994	99.99
Cobalt	380	1,030	ND< 0.4	> 99.96	> 99.91
Copper	1,320	3,710	1.4	99.96	99.91
Lead	140	307	1	99.7	99.4
Manganese	6,890	26,100	16	99.93	99.8
Mercury	8.35	16.1	9.64	62	--
Molybdenum	161	473	2.04	99.54	98.1
Nickel	593	16,130	ND< 0.4	> 99.97	> 99.94
Selenium	118	423	ND< 0.054	> 99.98	> 99.96
Vanadium	2,920	8,140	1.5	99.98	99.96

Table 3.3-3 Stream Temperatures, Springerville Station

Temperature, deg F	
SDA Inlet	290
SDA Outlet	167
Baghouse Inlet	179
Baghouse Outlet	177

Section 3.4 Cardinal Station

Ohio Power Company's Cardinal Station is located in Brilliant, Ohio, along the Ohio River. It has three coal-fired boilers and is adjacent to the TIDD pressurized fluidized bed combustor (PFBC) demonstration plant. Unit 1, the host site, is considered to be representative of older coal-fired power plants without NO_x or SO_2 controls and was operated at maximum capacity (606 MWe average) during the tests. Further, this unit is considered to be representative of cell burner boiler designs utilizing an electrostatic precipitator to control particulate emissions. These units are presently exempt from Phase 1 acid rain controls because the effectiveness of existing NO_x control technologies for this application is not well known. Babcock and Wilcox is the only manufacturer of cell burner units. This design was sold from 1960 to 1970.

The only atypical feature of the Cardinal boiler design is that the upper row of burners employs only a single nozzle. This feature is likely due to the lack of a spare pulverizer (all five must be in service to achieve full load) on this unit. Since NO_x emissions from the host unit are fairly typical of other cell burner units, it is believed that combustion conditions within the furnace are representative of most cell burner units despite this difference.

The plant fires a high-sulfur bituminous coal. This is typical of coals normally fired at the plant. The coal is a Pittsburgh No. 8 coal and is typical of medium volatile bituminous coals. The coal is shipped to the station by rail, barge, or truck. Coal is unloaded and stored at the plant in piles located between Units 1 and 2, and Unit 3. The coal for Unit 1 is delivered to five 600-ton bunkers by a series of conveyors without additional size reduction. At maximum firing rate, Unit 1 burns approximately 225 U.S. tons per hour. Coal from the bunkers is delivered to five bowl-mill pulverizers. The pulverized coal is pneumatically conveyed by the primary air to the boiler. Rejects (mainly pyrites

and other hard mineral matter) from the pulverizers are collected in bins at the base of the pulverizers.

The boiler is a forced-draft cell burner unit with two stages of reheat, manufactured by Babcock and Wilcox. Cell burner boilers are characterized by relatively small furnaces, resulting in a heat release per unit furnace volume of 6.7 MW/cubic meter. Downstream of the pulverizers, the air/coal mixture from each pipe is split into two pipes, either feeding separate burners at the top burner level or the two nozzles of a cell burner. Gaseous combustion products and entrained solids pass through the boiler and a single convective pass prior to splitting off to two vertical-axis regenerative rotary air preheaters.

Downstream of the air heaters are two Research-Cottrell ESPs (identified as A and B) arranged in parallel for particulate control. Each ESP has 10 fields in series. The ESP is moderately sized and has a design-specific collection area of 83 $m^2/m^3/sec$ (424 $ft^2/1000$ acfm). Electromechanical rappers are employed for discharge and collecting electrodes. Underneath each of the ESPs are three rows of six hoppers for collection of captured fly ash. Flue gas is exhausted to the atmosphere from a single round stack with a height exceeding 800 feet.

Ash Handling and Disposal

Bottom ash falls into the ash hopper at the base of the boiler. The bottom ash hoppers are sluiced by water four times a day forming a slurry of ash and water. The sluice cycle lasts one to two hours. Water for the slurry is supplied from the ash water recirculating pump pond from the Ohio River, and the slurry discharges to the bottom ash pond.

The fly ash collected in the ESP hoppers is removed with a vacuum pneumatic conveying system. A vacuum line from a water-driven eductor (hydroveyor) runs to all the hoppers. Each row of hoppers can be isolated by an automated valve at the head of each line.

The fly ash hoppers are evacuated sequentially in a continuous automatic cycle. The air is removed from the fly ash slurry downstream of the hydroveyor in an air/water separator tank. The slurry is then pumped from the tank and discharged to the fly ash settling pond.

A schematic flow diagram is shown in Figure 3.4-1 while Figure 3.4-2 presents the trace element partitioning. Tables 3.4-1 and 3.4-2 show the trace element flow rates and concentration/removal efficiencies for plant equipment. Table 3.4-3 gives the stream temperatures at various points in the plant.

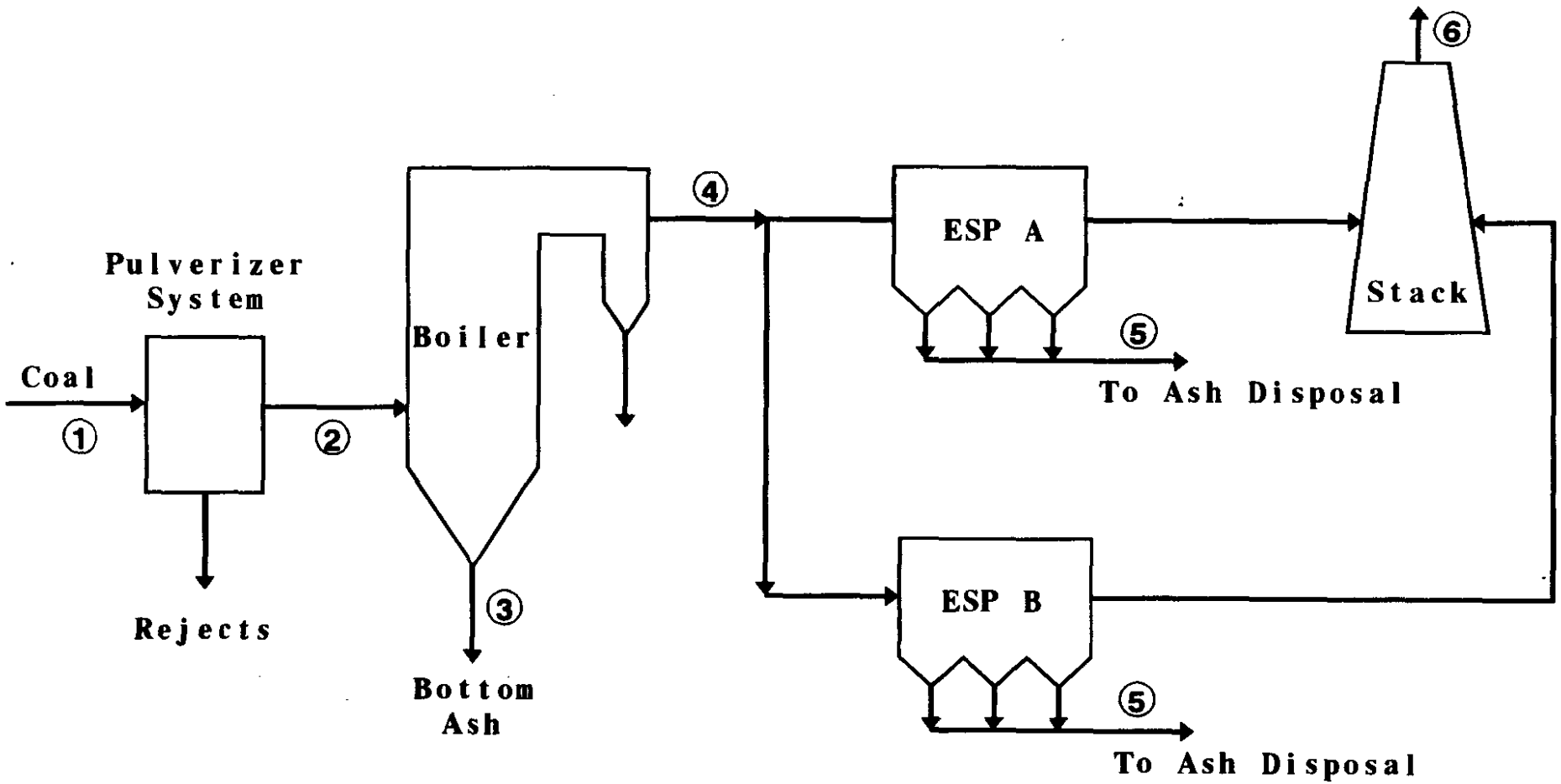

FIGURE 3.4-1. UNIT 1 FLOW DIAGRAM - CARDINAL STATION

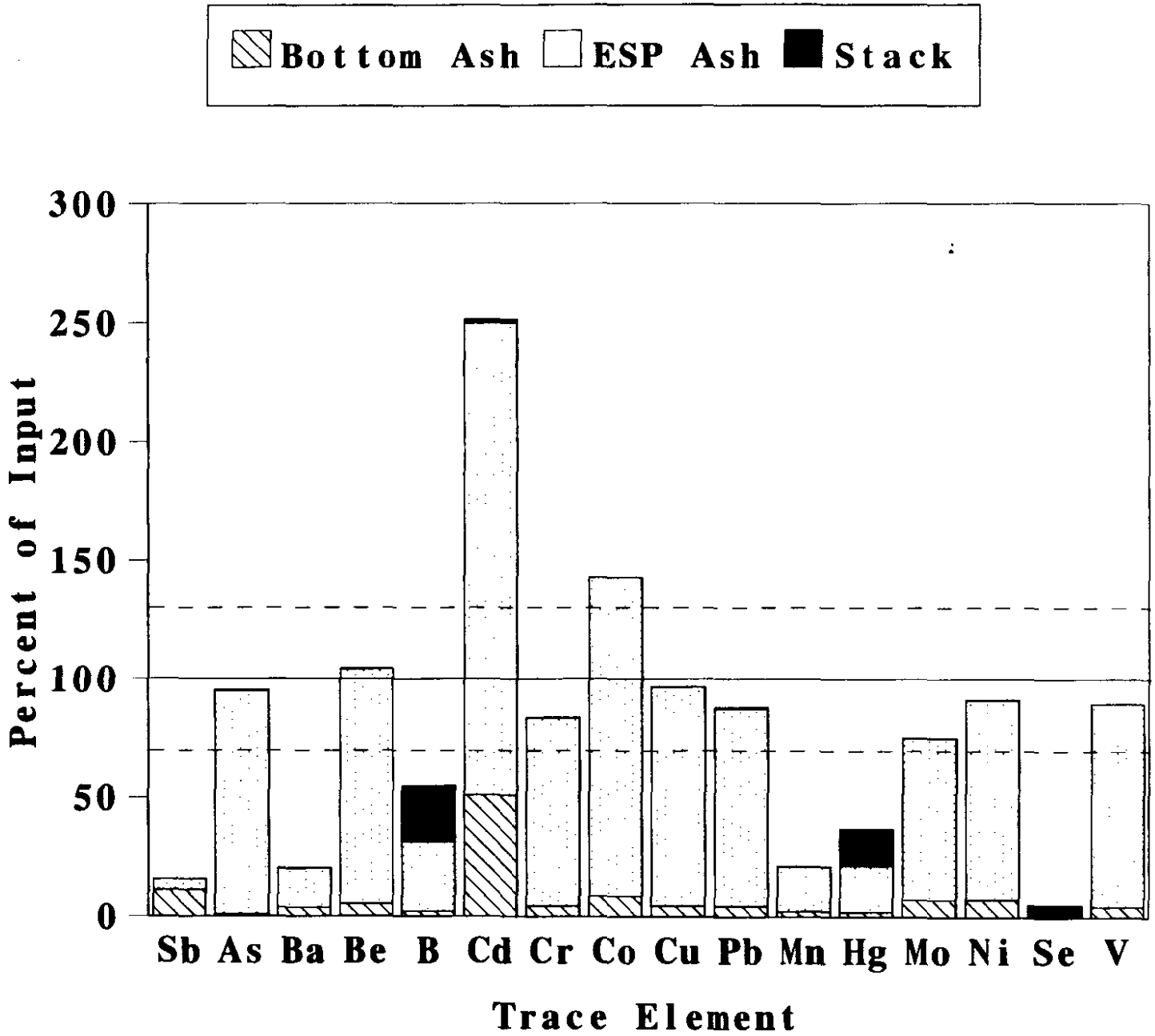

FIGURE 3.4-2. TRACE ELEMENTS IN OUTPUT STREAMS CARDINAL STATION

Table 3.4-1 Trace Elements Flow Rates, Cardinal Station

	(1) Coal Feed	(2) Bottom Ash	(3) Sluice Input	(4) ESP In	(5) ESP Ash	(6) Stack
Units: lb/hr						
Antimony	8.86	1.01	0.147	0.763	0.401	0.0100
Arsenic	5.38	0.057	0.059	5.31	5.06	0.0137
Barium	9.37	0.364	0.112	3.05	1.56	0.0039
Beryllium	0.55	0.030	0.0015	0.580	0.549	0.0003
Boron	41.0	0.908	0.227	24.1	12.1	9.6
Cadmium	0.254*	0.130	0.0006	0.168	0.507	0.0040
Chromium	7.52	0.340	0.0047	5.09	5.94	0.0255
Cobalt	1.87	0.165	0.015	1.96	2.53	0.0025
Copper	3.81	0.177	0.032	1.73	3.54	0.0065
Lead	2.82	0.129	0.013	3.22	2.35	0.0196
Manganese	24.0	0.586	0.175	6.90	4.50	0.0927
Mercury	0.02	0.0004	0.0003	0.0062	0.0040	0.0032
Molybdenum	1.35	0.101	0.015	0.831	0.925	0.0023
Nickel	5.95	0.452	0.040	4.89	5.01	0.0172
Selenium	9.63	0.015	0.0045	0.688	0.076	0.4145
Vanadium	13.5	0.604	0.0076	11.2	11.5	0.0061

*Calculated from crushed coal analysis.

Table 3.4-2 Concentration and Removal Efficiencies, Cardinal Station

	ESP A Inlet, µg/Nm³	ESP B Inlet, µg/Nm³	Stack, µg/Nm³	ESP Removal Efficiencies, Percent
Antimony	157	196	3.06	98.46
Arsenic	1,140	1,320	4.49	99.67
Barium	410	1,020	1.14	99.84
Beryllium	130	137	0.0899	99.93
Boron	5,590	5,510	2,470	56.30
Cadmium	17.1	62.3	1.1	97.18
Chromium	1,200	1,140	9.76	99.07
Cobalt	442	462	0.815	99.82
Copper	409	387	1.79	99.55
Lead	724	761	4.96	99.43
Manganese	2,220	928	19.3	96.82
Mercury	1.87	0.951	0.563	18.60
Molybdenum	192	189	0.758	99.53
Nickel	1,110	1,140	6.15	99.37
Selenium	135	183	120	19.03
Vanadium	2,470	2,700	2.05	99.93

Table 3.4-3 Stream Temperatures, Cardinal Station

Temperature, deg F	
Steam	994
ESP	330
Stack	327

Section 3.5 Baldwin Station

Plant Description

The Baldwin Power Station is located in Baldwin, Illinois, and is owned and operated by Illinois Power Company. The power plant is composed of three coal-fired units numbered 1 through 3. All three units are rated at 568 MWe. Unit 2 was studied in this program. This Babcock & Wilcox cyclone furnace unit, built in 1973, burns high-sulfur Illinois bituminous coal that is delivered to the station by train. Average coal characteristics for this study were 10.2% ash, 2.9% sulfur, 15.0% moisture, and 10,600 Btu/lb higher heating value.

Unit 2 is operated from a control room which is common to all three units. At Unit 2, coal is transferred from storage bunkers through feeders directly into 14 cyclones. The boiler is opposed-fired with a bottom row of four cyclones and a top row of three cyclones on each side. The combustion gases exit the furnace and enter the convective pass section of the boiler which includes superheater and reheater sections. Main and reheat steam temperatures are controlled primarily by flue gas recirculation and combustion air flow, and attemperation sprays for secondary control. Next, the combustion gases are directed through an economizer section.

Some entrained particulate (i.e., soot) is deposited on various boiler wall and tube surfaces. Unit 2 is equipped with a series of soot blowers to remove this slagging and fouling material. The soot blowers are used on a regular basis, once per shift. Supplemental soot blowing is performed to clean surfaces and regain optimum steam temperature control and thermal efficiency when heat absorption patterns change.

Some overhead particulate is collected at the economizer outlet and is conveyed to an ash pond via a water sluice system. Final

particulate control is effected by an electrostatic precipitator (ESP). The ESP ash is also sluiced to an ash pond.

The ESP consists of six chambers and each chamber is four fields deep. The ESP has a specific collection area of 179.8 ft^2/1,000 cfm and uses weighted wire electrodes. The collecting plates are spaced 9 inches apart. Unit 2 has no other pollution control equipment.

The unit has its own stack. Ports at the ESP inlet and outlet (stack) were used for flue gas emission sampling/testing purposes.

The unit's condenser system is a tube heat exchanger. The average intake rate of condenser water is 50 ft^3/s. This system is served by a cooling reservoir (Baldwin Lake) covering an area of 2,000 acres and containing 22,000 acre feet of water.

The bottom ash, economizer hopper ash, and ESP hopper ashes are sluiced to an on-site ash pond system. The bottom ash is sluiced to its own primary and secondary ponds. The economizer and ESP hopper ashes are sluiced to common primary and secondary ponds. The supernatant from both secondary ponds overflows to a single tertiary pond. The effluent from the tertiary pond is discharged to the nearby Kaskaskia River. All of the bottom ash is sold for commercial use.

A process flow diagram of Baldwin Unit 2 is shown in Figure 3.5-1. Figures 3.5-2 and 3.5-3 give the partitioning results for non-soot-blowing and soot-blowing periods. Tables 3.5-1 and 3.5-2 present trace element flow rates for both periods. Table 3.5-3 presents the concentration and removal efficiency results for both periods. Table 3.5-4 gives stream temperatures at various points in the plant.

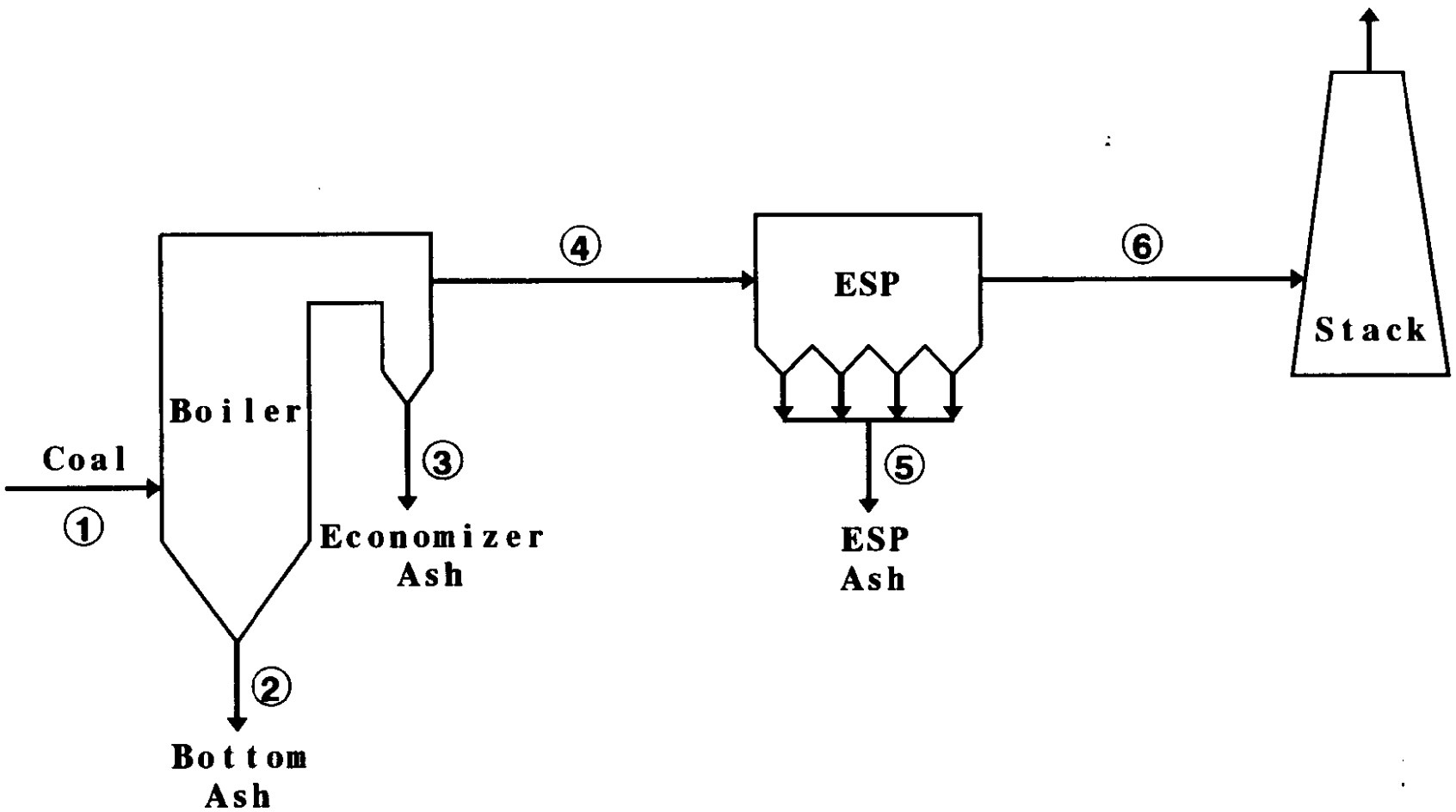

FIGURE 3.5-1. BALDWIN POWER STATION UNIT NO. 2 FLOW DIAGRAM

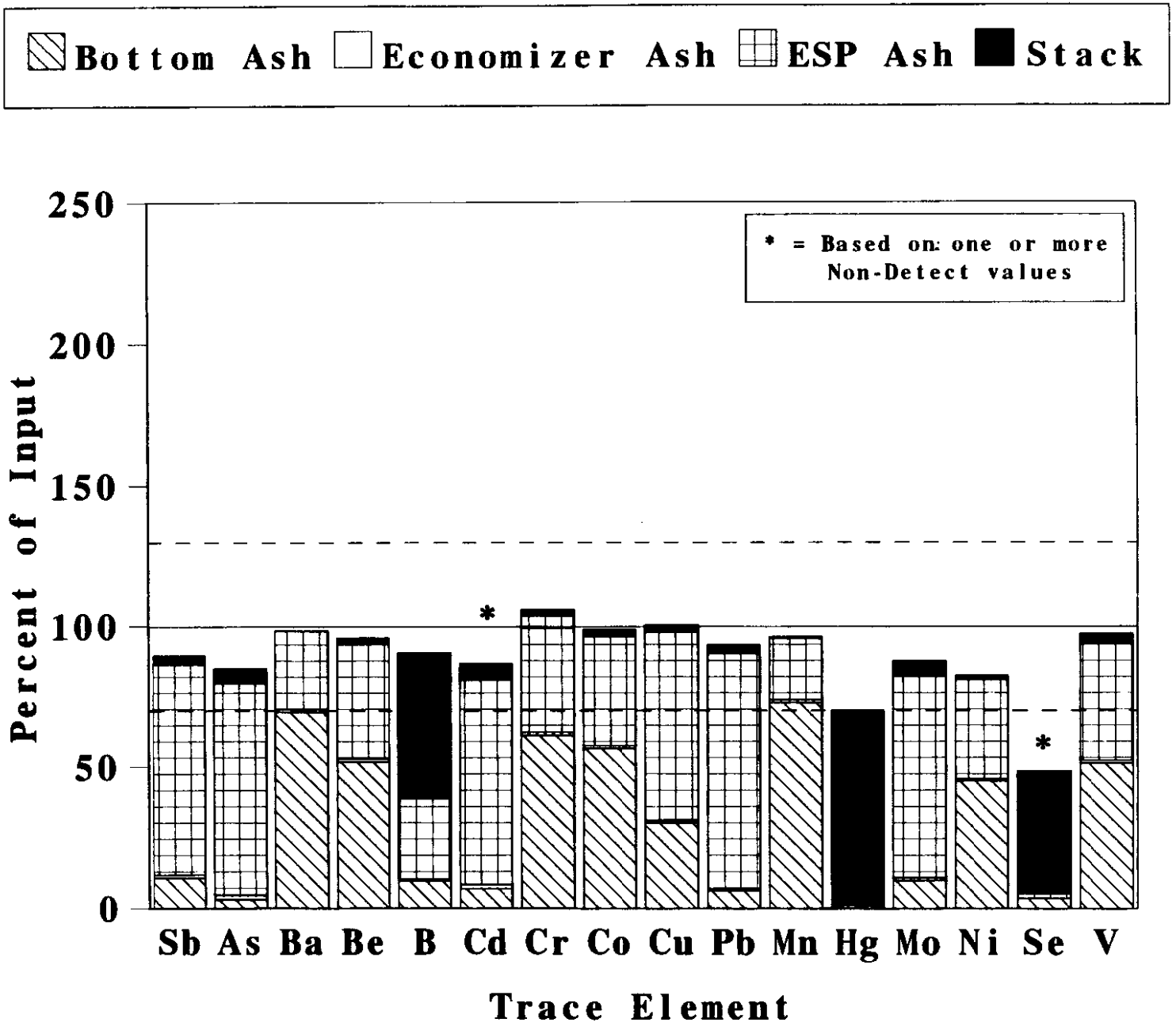

FIGURE 3.5-2. TRACE ELEMENTS IN OUTPUT STREAMS BALDWIN STATION, NON-SOOT BLOWING TESTS

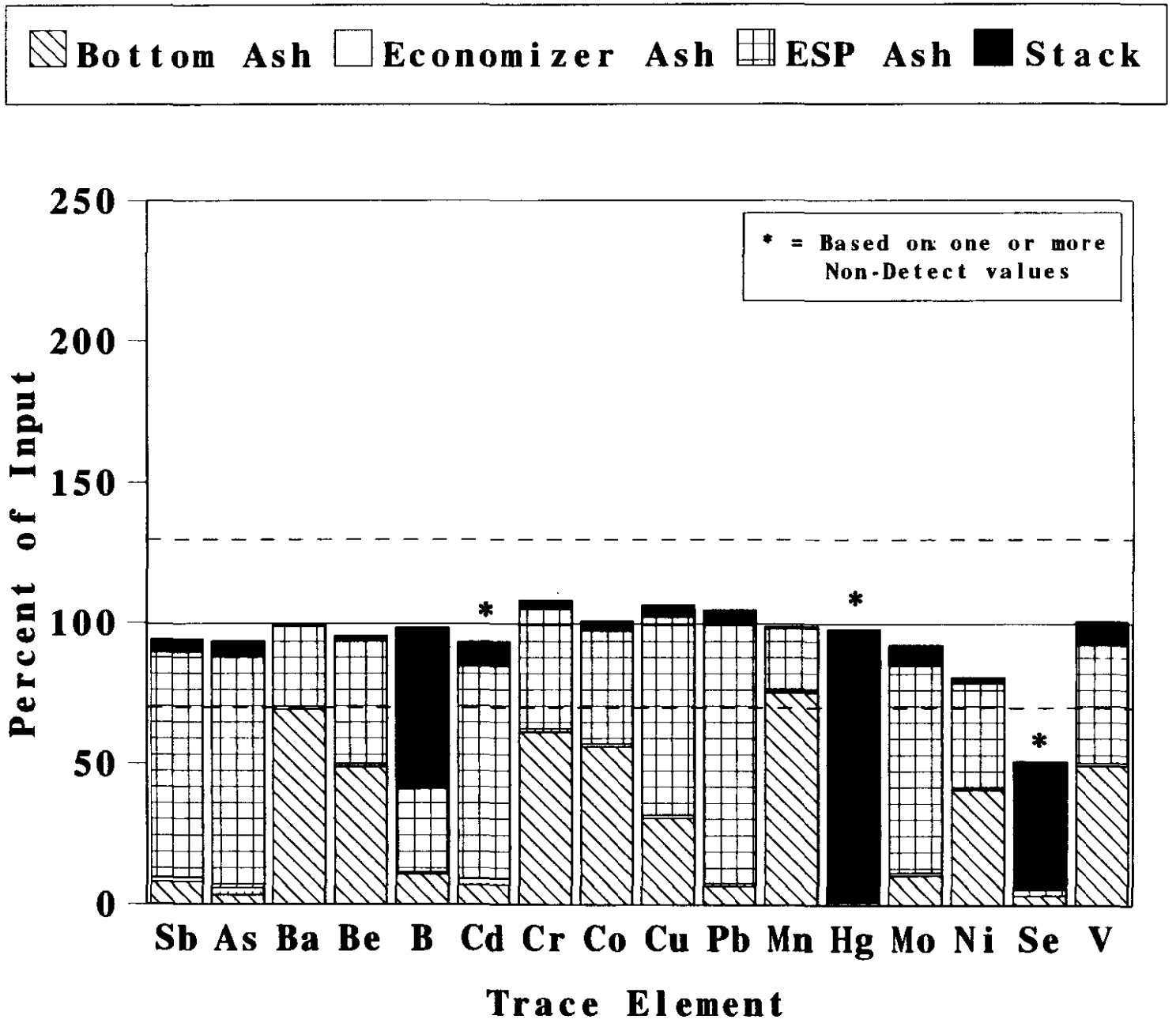

FIGURE 3.5-3. TRACE ELEMENTS IN OUTPUT STREAMS BALDWIN STATION, SOOT BLOWING TESTS

Table 3.5-1 Trace Element Flow Rates, Baldwin Station, Non-Soot Blowing Period

	(1) Coal Input	(2) Bottom Ash	(3) Economizer Ash	(4) ESP Inlet	(5) ESP Ash	(6) Stack
Units: lb/hr						
Antimony	0.263	0.028	0.0028	0.084	0.196	0.0087
Arsenic	1.43	0.044	0.024	5.7	1.07	0.077
Barium	27.6	19.2	0.288	5.9	7.671	0.030
Beryllium	0.539	0.279	0.0055	0.24	0.224	0.0081
Boron	85.2	8.22	0.527	220	24.3	44.
Cadmium	0.290	ND< 0.020 #	0.0044	0.38	0.210	0.017
Chromium	13.3	8.11	0.156	5.5	5.48	0.29
Cobalt	1.68	0.948	0.017	0.81	0.654	0.039
Copper	4.48	1.35	0.042	2.8	2.99	0.11
Lead	5.02	0.320	0.037	2.7	4.17	0.16
Manganese	21.7	15.8	0.232	4.4	4.72	0.13
Mercury	0.032	0.0004[B]	0.00001	0.030	0.0002[A]	0.022
Molybdenum	3.38	0.333	0.031	2.1	2.40	0.19
Nickel	8.39	3.76	0.071	3.6	2.94	0.13
Selenium	1.72	ND< 0.061 #	ND< 0.001 #	0.071	ND< 0.029 #	0.74
Vanadium	15.6	8.00	0.157	7.6	6.46	0.57

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.5-2 Trace Element Flow Rates, Baldwin Station, Soot Blowing Period

	(1) Coal Input	(2) Bottom Ash	(3) Economizer Ash	(4) ESP Inlet	(5) ESP Ash	(6) Stack
Units: lb/hr						
Antimony	0.263	0.021	0.0040	0.220	0.210	0.012
Arsenic	1.43	0.049	0.034	7.90	1.18	0.070
Barium	27.6	19.1	0.292	9.80	7.89	0.019
Beryllium	0.539	0.263	0.0056	0.380	0.236	0.010
Boron	85.2	9.00	0.701	320	25.1	49.0
Cadmium	0.290	ND< 0.020 #	0.0067	0.670	0.219	0.025
Chromium	13.3	8.11	0.181	9.50	5.65	0.390
Cobalt	1.68	0.941	0.018	1.40	0.678	0.057
Copper	4.48	1.37	0.050	4.80	3.16	0.190
Lead	5.02	0.331	0.054	5.20	4.60	0.270
Manganese	21.7	16.4	0.237	7.30	4.72	0.180
Mercury	0.032	ND< 0.0004 #	0.00001	0.040	0.0002[A]	0.031
Molybdenum	3.38	0.350	0.035	3.30	2.48	0.240
Nickel	8.39	3.42	0.080	6.20	3.09	0.180
Selenium	1.72	ND< 0.060 #	ND< 0.0010 #	0.080	0.028[C]	0.780
Vanadium	15.6	7.70	0.173	13.0	6.55	1.30

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling in two hoppers)
Non-detectible in all samples

Table 3.5-3 Concentrations and Collection Device Removal Efficiencies, Baldwin Station

	Non-Soot Blowing			Soot Blowing		
	ESP Inlet, µg/Nm³	ESP Outlet, µg/Nm³	Removal Efficiency, Percent	ESP Inlet, µg/Nm³	ESP Outlet, µg/Nm³	Removal Efficiency, Percent
Antimony	19	2.1	89.6	50	2.8	94.6
Arsenic	1,300	18	98.7	1,900	17	99.1
Barium	1,400	7.2	99.5	2,300	4.6	99.8
Beryllium	55	1.9	96.6	89	2.3	97.4
Boron	50,000	10,000	79.8	74,000	12,000	84.8
Cadmium	88	4.1	95.5	160	6.0	96.2
Chromium	1,300	69	94.7	2,200	92	95.9
Cobalt	190	9.3	95.2	320	13	95.8
Copper	650	26	96.1	1,100	44	96.1
Lead	610	39	93.9	1,200	64	94.7
Manganese	1,000	30	97.1	1,700	43	97.5
Mercury	6.8	5.2	26.0	9.5	7.2	24.4
Molybdenum	490	46	90.9	780	56	92.9
Nickel	840	30	96.5	1,400	42	97.1
Selenium	16	180		18	190	
Vanadium	1,800	140	92.4	3,000	300	90.1

Table 3.5-4 Stream Temperatures, Baldwin Station

Temperature, deg F	
Non-Soot Blowing	
ESP Inlet	336
ESP Outlet (To Stack)	336
Soot Blowing	
ESP Inlet	329
ESP Outlet (To Stack)	332

Section 3.6 Niles Station

Niles Station of Ohio Edison is located in Niles, Ohio, on the bank of the Mahoning River. The Niles Boiler No. 2 is a Babcock & Wilcox cyclone boiler burning bituminous coal with a net generating capacity of 108 MWe. The furnace gas temperature at full load upstream of the superheater is about 1900°F. The boiler has four cyclone burners, each fed by a separate feeder. The Niles Plant uses coal with a low ash fusion temperature to allow the majority of the ash to drop out in the furnace cyclone combustors and to avoid carry-over into the boiler. The coal is mined in eastern Ohio and western Pennsylvania and is received in the respective proportions of about 70/30. Coal mined in Ohio comes principally from coal seams Nos. 6 and 7. The Pennsylvania mined coal comes also from seams Nos. 6 and 7 and from the Kittanning/Freeport seam. All the coal burned at the plant is from spot market purchases which are provided by up to a dozen different suppliers. The nominal contents of sulfur, ash, and higher heating value are 2.7 percent, 10-12 percent, and 12,000 Btu/lb, respectively. The coal is blended in the coal yard at the plant to meet 24-hour and 30-day rolling averages for SO_2 content of flue gas. The feed rate of crushed coal to the four cyclone burners is determined by Ohio Edison from the quantity of coal on the four conveyor belts delivering the coal to the burners, along with the speed of travel of the belts. Each belt holds approximately 45 kg/m (30 lb/ft) of coal. The lag time for coal on each of the four conveyor belts to reach the cyclone burners and be fired is a few minutes.

The flue gas leaves the boiler economizer, passes through an air heater (not shown), and enters an electrostatic precipitator (ESP) with five fields, each with two hoppers. The first row of hoppers is deactivated and acts to passively collect coarse ash leaving the air heater. The fourth row of hoppers was also deactivated during this study, but was sampled. The ESP hoppers are dumped about every 4 hours; hopper sampling in this study was adapted to that

schedule. The proportions of ash collected in each row of hoppers were estimated during this study by timing of the dumping cycle of the ESP. Collected ESP ash is transported to a settling pond by a water sluice. The flue gas leaving the ESP is vented through a 120-m (393-foot) tall stack.

Characteristic of cyclone boilers, a large fraction of the ash from coal combustion is collected as bottom ash and relatively little as fly ash. For Niles Boiler No. 2, typically about 85 percent of the total ash is collected as bottom ash and air heater ash (of that portion the great majority is bottom ash), and only about 15 percent of the total ash is collected in the ESP. The fly ash produced by a cyclone boiler typically is relatively coarse and has a larger carbon content than does such ash from other boiler designs. The typical average carbon content of the ash collected in the entire ESP is about 40 percent at Niles Boiler No. 2. The coarse nature of the fly ash is the reason that the row 1 ESP hoppers are operated as passive (i.e., deenergized) collectors.

A 35-megawatt equivalent slipstream of flue gas from the Niles Boiler No. 2 is normally taken after the air heater and before the ESP to demonstrate the SNOX process, an ICCT demonstration by ABB Combustion Engineering. The SNOX process was shut down during the sampling period described here so that 100 percent of the Boiler No. 2 flue gas passed through the ESP before venting through the stack.

Ammonia is normally added to the flue gas upstream of the ESP at a rate of 0.1-0.2 m^3/min (4-6 cubic feet per minute) to achieve a concentration of about 18 ppm. This is done to control acid mist fallout from the stack and does not appreciably affect ESP performance. However, during the course of this project ammonia was not added to the flue gas to assure consistency with separate measurements made as part of another program on the SNOX process in which ammonia was not added.

Normally, soot blowing occurs once each shift. To accommodate measurements of the effect of soot blowing on flue gas element concentrations, Ohio Edison altered the schedule for soot blowing during the field study. Soot blowing was conducted over a 2-hour period (approximately 6-8 a.m.) before sampling began each day and again after all sampling was completed each day. Soot blowing is conducted automatically using 18 lances sequentially, one at a time. Seventeen of the lances are located in the furnace gas convection path, and one is located at the top of the air heater. Compressed air is used for soot blowing.

A schematic of the Niles Boiler No. 2 process flow is shown in Figure 3.6-1. Figure 3.6-2 presents the partitioning of the elements which give the trace element flow rates. Table 3.6-2 shows concentrations and removal efficiencies at key points in the plant. Gas stream concentrations are reported on a dry basis, corrected to 3% oxygen. Table 3.6-3 gives stream temperatures at various points in the plant.

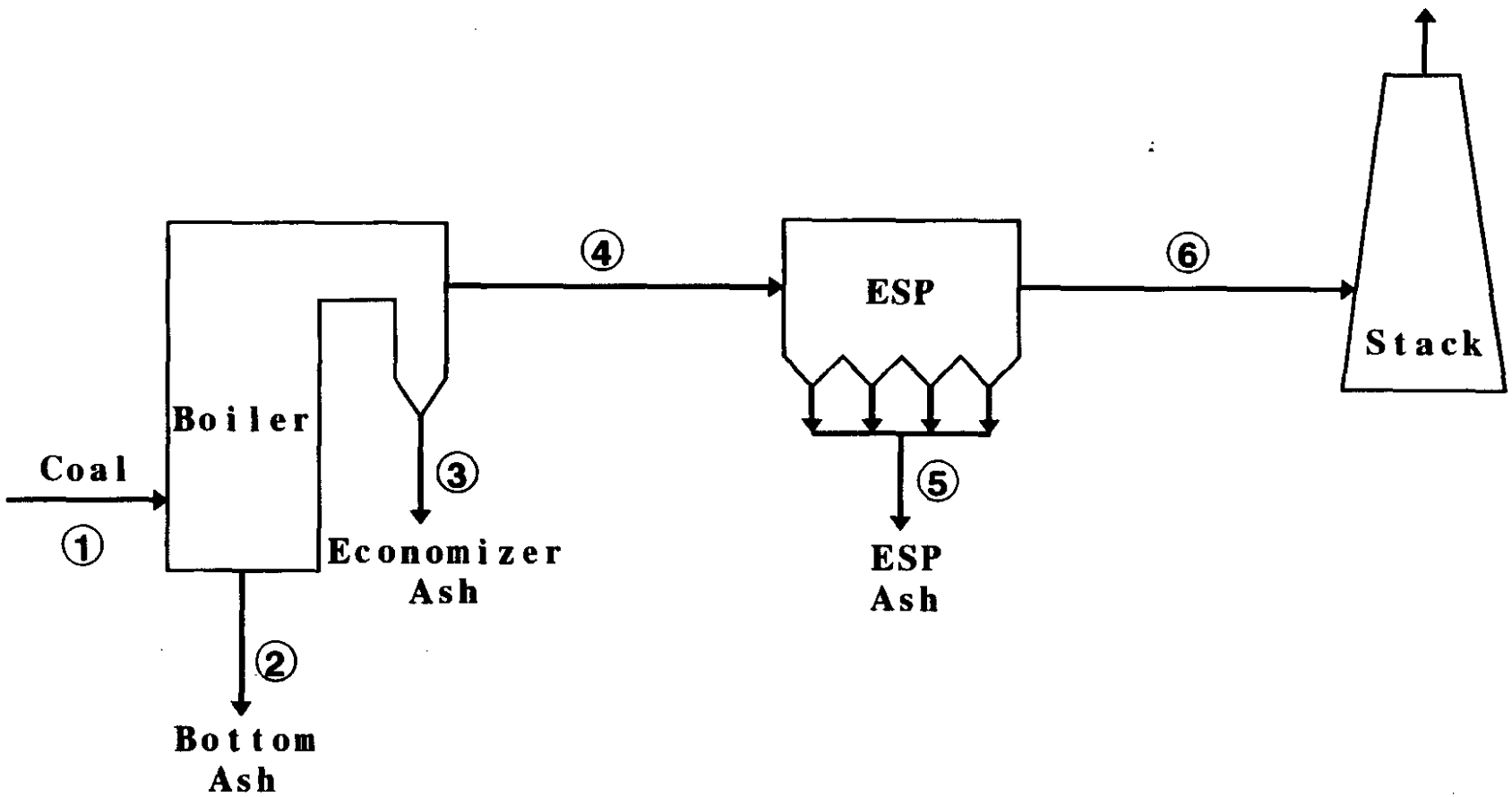

FIGURE 3.6-1. NILES STATION BOILER NO. 2 FLOW DIAGRAM

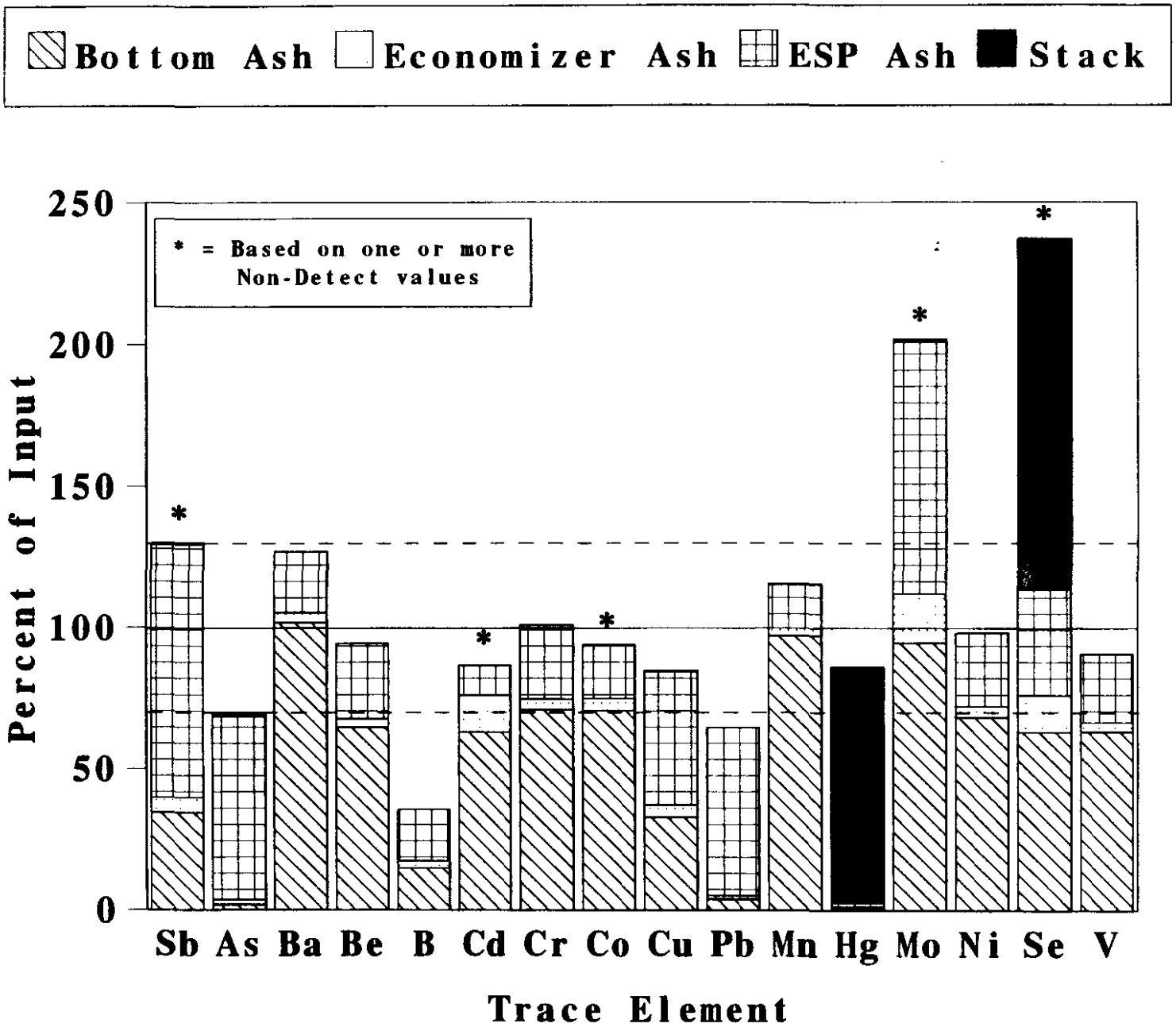

FIGURE 3.6-2. TRACE ELEMENTS IN OUTPUT STREAMS NILES STATION

Table 3.6-1 Trace Element Flow Rates, Niles Station

	(1) Coal	(2) Bottom Ash	(3) Economizer Ash	(4) ESP Inlet	(5) ESP Ash	(6) ESP Out, Stack
Units: lb/hr						
Antimony	0.104	ND< 0.0356 #	ND< 0.0055 #	0.126	ND< 0.0930 #	ND< 0.0004 #
Arsenic	3.11	0.0569	0.0566	1.88	2.01	0.0479
Barium	5.18	5.27	0.183	0.933	1.11	0.0060
Beryllium	0.179	0.116	0.0055	0.0487	0.0474	0.0002
Boron	6.78	1.00	0.170	N/A	1.23	N/A
Cadmium	ND< 0.0282 #	ND< 0.0178 #	ND< 0.0037 #	0.0031	ND< 0.0029 #	ND< 0.00007[B]
Chromium	1.51	1.07	0.0566	0.435	0.394	0.0035
Cobalt	0.593	0.418	0.0256	0.124	0.113	ND< 0.0001 #
Copper	1.41	0.462	0.0603	0.687	0.667	0.0046
Lead	1.22	0.0471	0.0152	0.704	0.726	0.0018
Manganese	2.35	2.29	0.0621	0.383	0.366	0.0038
Mercury	0.0198	0.0002[B]	0.0001	0.0231	0.0003	0.0164[B]
Molybdenum	ND< 0.282 #	ND< 0.267 #	ND< 0.0493 #	0.135	ND< 0.251 #	0.0025
Nickel	1.69	1.16	0.0658	0.511	0.439	0.0006
Selenium	ND< 0.0565 #	ND< 0.0356 #	0.0073[B]	0.0752	0.0212[B]	0.0698
Vanadium	2.64	1.66	0.0859	0.668	0.636	0.0029

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples
N/A Not analyzed

Table 3.6-2 Concentrations and Removal Efficiencies, Niles Station

	ESP Inlet, $\mu g/Nm^3$	Stack, $\mu g/Nm^3$	ESP Removal Efficiency, Percent
Antimony	152	ND< 0.60 #	99.8
Arsenic	2,274	70	97.4
Barium	1,129	8.8	99.3
Beryllium	59	0.31	99.6
Boron			
Cadmium	3.7	ND< 0.10^B	97.1
Chromium	526	5.1	99.2
Cobalt	150	ND< 0.20 #	99.95
Copper	831	6.7	99.3
Lead	852	2.7	99.7
Manganese	463	5.6	99.0
Mercury	28	24	29.9
Molybdenum	163	3.7	98.1
Nickel	618	0.9	99.9
Selenium	91	102	7.6
Vanadium	808	4.2	99.6

A Includes one non-detect measurement
B Includes two non-detect measurements
Non-detectible in all samples

Table 3.6-3 Stream Temperatures, Niles Station

Temperature, deg F	
Steam, Superheater Outlet	1000
Steam, Reheater Outlet	987
ESP Inlet	304
ESP Outlet (To Stack)	293

Section 3.7 SNOX Process

Niles Station of Ohio Edison is located in Niles, Ohio. The Niles Boiler No. 2 is a cyclone boiler burning bituminous coal with a net generating capacity of 100 MWe. The boiler has four cyclone burners, each fed by a separate feeder. Nominal sulfur content of the coal is 2.8 percent. The coal comes from several local sources and is blended in the coal yard to meet 24-hour and 30-day rolling averages for SO_2 content of flue gas.

The flue gas leaves the boiler, passes through an air heater (not shown), and enters an electrostatic precipitator (ESP) with five fields, each with two hoppers. The flue gas leaving the ESP is vented through a 120-m (393-foot) tall stack.

The SNOX process takes a slipstream of flue gas ahead of the ESP, cleans the slipstream, and returns it to the flue gas after the ESP and before the stack. All flue gas sampling was conducted on the slipstream of the SNOX process. Therefore, operation of the ESP had no effect on the measurements summarized in this report.

This ICCT project is the Wet Gas Sulfuric Acid (WSA)-Selective Catalytic Reduction of NO_x (SNOX) demonstration by ABB Environmental Systems (*Comprehensive Report to Congress, Clean Coal Technology Program, WSA-SNOX Flue Gas Cleaning Demonstration Project*, U.S. Department of Energy Report No. DOE/FE-0151, November 1989). Cosponsors are DOE, Ohio Coal Development Office, Ohio Edison, and Snamprogetti, USA. The SNOX process combines selective catalytic reduction and wet sulfuric acid technologies to remove both nitrogen and sulfur oxides from flue gas.

A 35-MWe equivalent slip of flue gas from the Niles Boiler No. 2 is taken after the air preheater and before the ESP to demonstrate the SNOX process. The SNOX system pulls a constant load from Boiler No. 2 as the total load on the boiler fluctuates about full load.

The flue gas entering the SNOX process from Boiler No. 2 first passes through a support burner (not shown) to increase its temperature. The support burner is fueled with natural gas. The combustion air flow is steady, and the flow of natural gas is varied to maintain the temperature of the flue gas. The heated flue gas travels to a baghouse to remove particulate matter. After the flue gas leaves the baghouse, ammonia is added to the particulate-free flue gas. The flue gas then passes through the selective catalytic reduction (SCR) unit, where oxides of nitrogen are reduced to free nitrogen and water vapor. The flue gas then passes through the SO_2 reactor where SO_2 is oxidized catalytically to sulfur trioxide and subsequently recovered as sulfuric acid in a wet gas sulfuric acid condenser. The flue gas then rejoins the flue gas from the boiler downstream of the ESP, and exits through the stack.

The SNOX baghouse removes particulate matter from the flue gas stream prior to the SO_2 catalyst. This allows the catalyst, which collects and retains over 90 percent of the particulate matter reaching it, to be used for longer periods of time before cleaning.

The SNOX baghouse was manufactured by ABB Environmental Systems. With a gross air-to-cloth ratio of 3.76 (4.51 net), it has six compartments containing a total of 1,596 Gore-Tex bags. The bags are 431 cm long (169.75 inches) and 15.2 cm (6 inches) in diameter. The bag material is Teflon on fiberglass. New bags were installed in the baghouse several days before sampling began.

Collected particulate matter is dislodged from the bags by pulse jet cleaning several times an hour. The pulse pressure is 3.4-4.8 x 10^5 kPa (50-70 psi). This is automatically initiated by pressure drop sensors. The ash falls into one of six hoppers. The hoppers are dumped once a shift after the ESP hoppers are dumped. The Niles Station hydro-vac system first empties the ESP hoppers and then automatically empties the SNOX baghouse hoppers. Ash is drawn

out of the baghouse hoppers into a sluice line until the low vacuum limit is reached.

After the flue gas leaves the baghouse, it passes through a gas-gas heat exchanger (not shown), increasing the flue gas temperature. Ammonia is added to the flue gas on a local scale throughout the cross section of the duct through a matrix of nozzles. An additional 22.65 scm/min (800 scfm) of air flow is added to the flue gas with the ammonia addition. The ammonia/flue gas mixture enters the SCR and contacts the monolithic catalyst. The catalyst reduces the NO to nitrogen and water vapor. The local concentration ratio of ammonia/nitrogen oxides can be slightly greater than stoichiometric because any unreacted ammonia that passes out of the SCR is oxidized to NO, water and nitrogen further downstream in the SO_2 reactor. Throughout this portion of the SNOX process, the temperature of the flue gas is above the dew point of ammonium sulfate and ammonium bisulfate. Therefore, no sulfate particulate matter is generated in the flue gas from the ammonia.

The flue gas leaving the SCR is heated to increase its temperature for optimum conversion of SO_2 in the SO_2 reactor. The SO_2 is oxidized to SO_3 as it passes through a sulfuric acid catalyst.

The flue gas then passes through the gas-gas heat exchanger where SO_3 is hydrated to sulfuric acid. The sulfuric acid vapor is condensed in the WSA condenser. This is a tube and shell falling film condenser with ambient air used as a cooling medium on the shell side. The condenser has 7,200 glass tubes.

The condensed sulfuric acid is fed into an acid conditioning and storage system.

A flow diagram is shown in Figure 3.7-1. Figure 3.7-2 shows the partitioning of the trace elements. Tables 3.7-1 and 3.7-2 present the trace element flow rates and concentrations/removal

efficiencies, respectively. Table 3.7-3 gives the stream temperatures at various points in the plant.

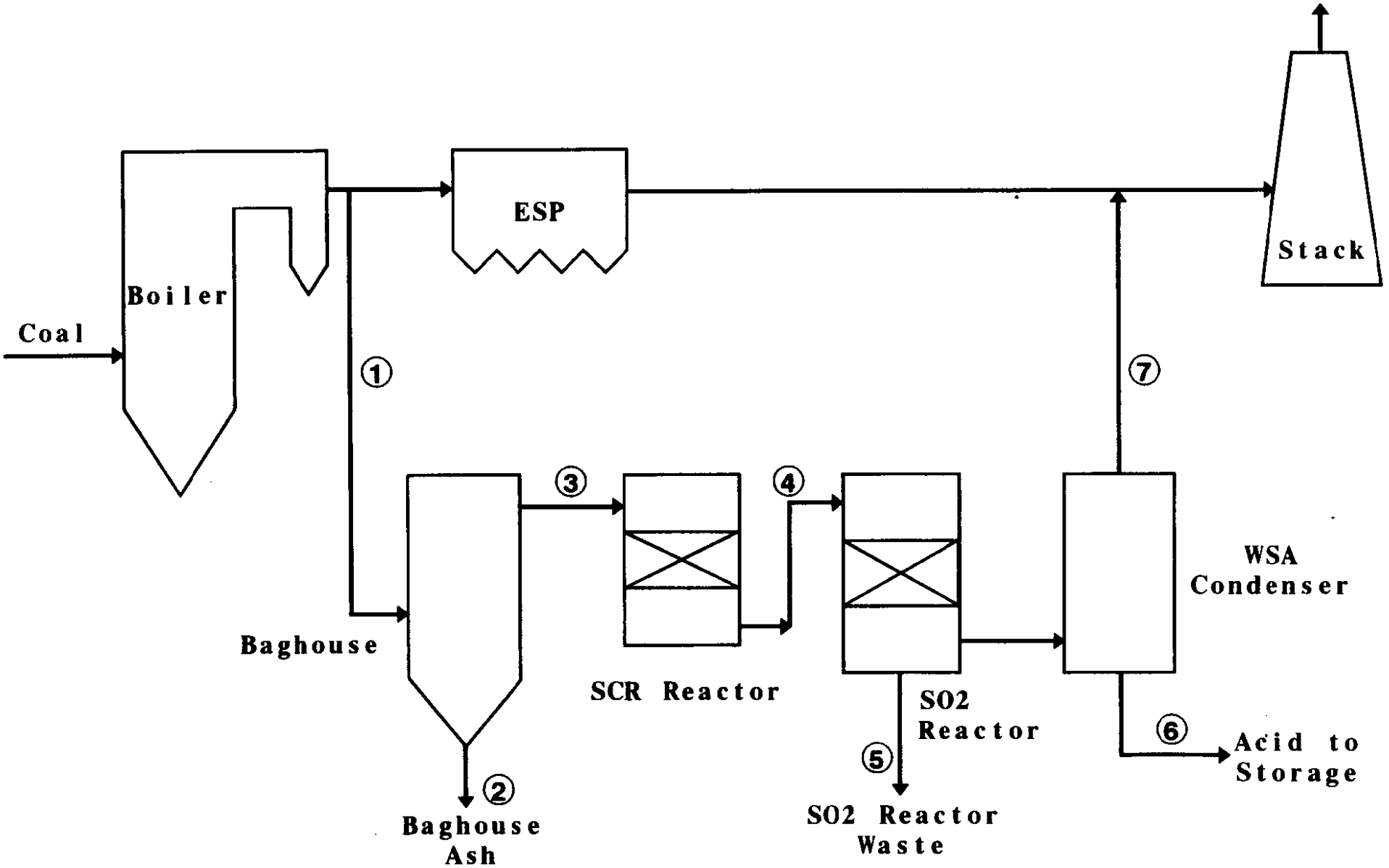

FIGURE 3.7-1. SNOX FLOW DIAGRAM

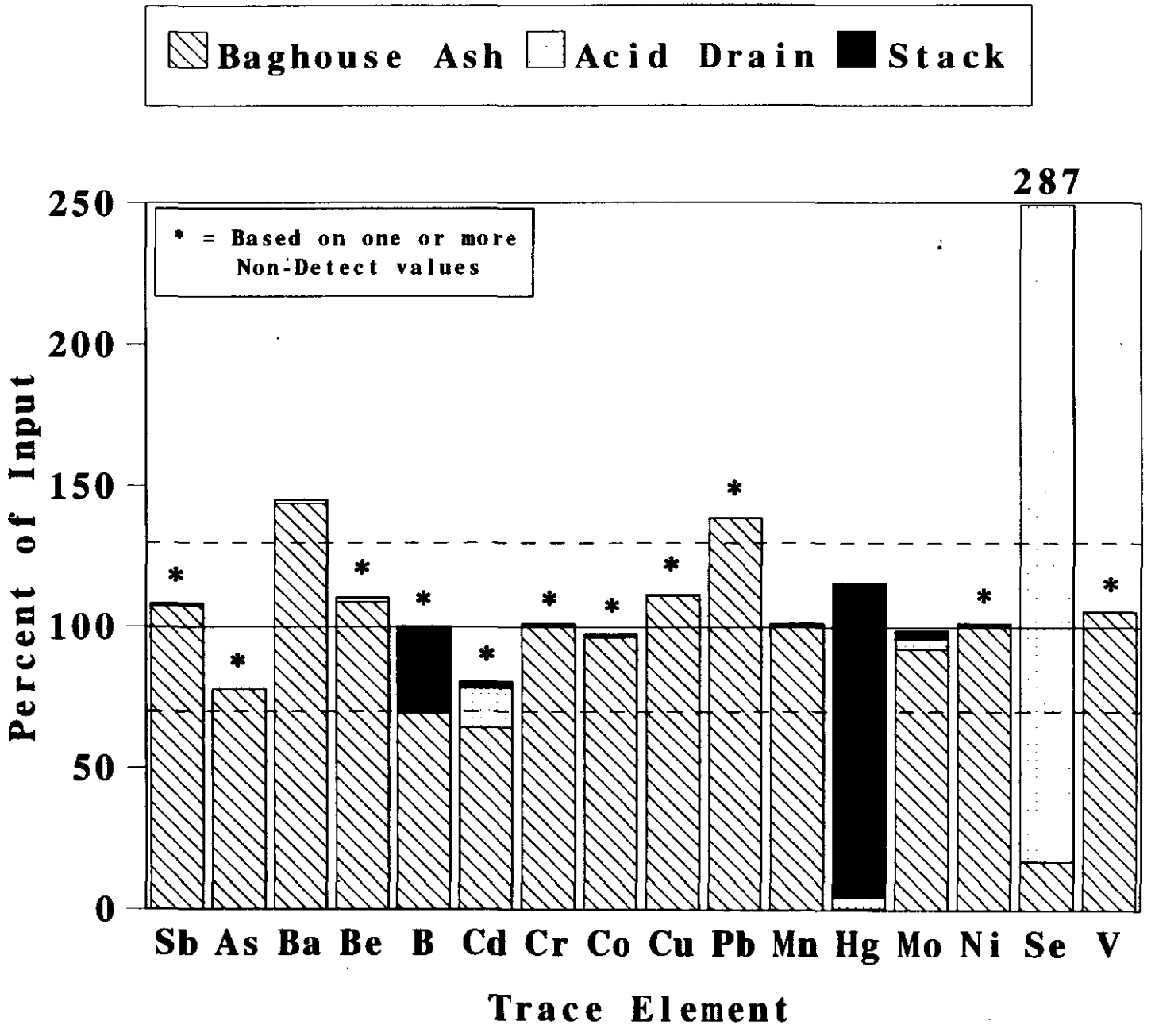

FIGURE 3.7-2. TRACE ELEMENTS IN OUTPUT STREAMS NILES STATION, SNOX PROCESS

Table 3.7-1 Trace Element Flow Rates, SNOX Process (Niles Station)

	(1) Slip Stream Inlet	(2) Baghouse Ash	(3) Baghouse Outlet	(4) SCR Outlet	(5) SO_2 Reactor Waste	(6) H_2SO_4 Drain	(7) Stack
Units: lb/hr							
Antimony	0.0213	0.0229	ND< 0.00011 #	ND< 0.00012 #	0	ND< 0.00004	ND< 0.00016 #
Arsenic	0.742	0.575	0.0029	0.0003[A]	0	0.0003	ND< 0.00016 #
Barium	0.302	0.434	0.0004	0.0002	0	0.0040	0.00006[B]
Beryllium	0.0175	0.0190	0.000018[B]	ND< 0.00004 #	0	ND< 0.00021 #	0.00005[A]
Boron	N/A	0.369	N/A	N/A	0	0.163	N/A
Cadmium	0.0015	0.0010[A]	ND< 0.00002 #	0.00004[B]	0	ND< 0.0002 #	ND< 0.00004[B]
Chromium	0.137	0.136	0.0004	0.0016	0	ND< 0.0002 #	0.0013
Cobalt	0.0461	0.0443	0.00004[B]	0.00009[B]	0	ND< 0.0004 #	ND< 0.00007[B]
Copper	0.199	0.221	0.0004	0.0038	0	ND< 0.0002 #	0.0003
Lead	0.201	0.279	0.0001[B]	0.0001[B]	0	ND< 0.00004 #	0.0002[B]
Manganese	0.133	0.133	0.0007	0.0019	0	0.0002[A]	0.0008
Mercury	0.0064	0.00004	0.0063	0.0070	0	0.0003	0.0070
Molybdenum	0.0608	0.0560	0.0005	0.0022	0	0.0021[B]	0.0018
Nickel	0.152	0.153	0.0001[A]	0.0006	0	ND< 0.0004 #	0.0007
Selenium	0.0236	0.0040	0.0192	0.0232	0	0.0635	0.0002
Vanadium	0.205	0.216	0.000009[B]	0.0001	0	ND< 0.0002 #	ND< 0.00004 #

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples
N/A Not Available

Table 3.7-2 Concentrations and Removal Efficiencies, SNOX Process (Niles Station)

	Baghouse Inlet, $\mu g/Nm^3$	Baghouse Outlet, $\mu g/Nm^3$	Stack, $\mu g/Nm^3$	Baghouse Removal Efficiencies, Percent	SNOX Removal Efficiencies, Percent
Antimony	94	ND< 0.48	ND< 0.69	99.7	99.6
Arsenic	3,270	13	ND< 0.69	99.6	99.99
Barium	1,330	1.7	0.24	99.9	99.98
Beryllium	77	ND< 0.08	0.23	99.9	99.7
Boron					
Cadmium	6.7	ND< 0.09	ND< 0.16	99.0	97.9
Chromium	602	1.7	5.4	99.3	99.1
Cobalt	203	ND< 0.17	ND< 0.30	99.96	99.9
Copper	875	1.6	1.2	99.8	99.9
Lead	888	0.52	0.73	99.95	99.9
Manganese	584	3.1	3.6	99.4	99.3
Mercury	28	28	30	--	--
Molybdenum	268	2.4	7.5	99.0	96.9
Nickel	669	0.31	3	99.95	99.6
Selenium	104	85	0.92	17	99.1
Vanadium	904	ND< 0.04	ND< 0.15	100	99.99

Table 3.7-3 Stream Temperatures, SNOX Process

Temperature, deg F	
Steam, Superheater Outlet	998
Steam, Reheater Outlet	974
Baghouse Inlet	387
Baghouse Outlet	379
SCR Oultet	663
WSA Condenser Inlet	505
WSA Condenser Outlet (To Stack)	196

Section 3.8 Plant Yates

The Plant Yates Unit No. 1 is a bituminous coal-fired steam electricity-generating unit with a net generating capacity of 100 MWe. Located in Newnan, Georgia, the station is owned and operated by Georgia Power Company. Unit 1 includes a tangentially fired CE boiler that burns a 2.5 % sulfur blend of Illinois No. 5 and Illinois No. 6 bituminous coals, an electrostatic precipitator for particulate control, and the CT-121 flue gas desulfurization system for sulfur dioxide (SO_2) emissions control during the ICCT demonstration.

Flue gas flows through a single duct into the ESP, which is four chambers wide and three rows of chambers deep; however, only the first two rows of chambers are energized. The ESP has a separate row of hoppers to collect the fly ash from each field, i.e., one row of hoppers per field. After the ESP, the flue gas flows through a single ID fan and then to the CT-121 system. The flue gas exiting the CT-121 unit is vented to the atmosphere through a 250-foot exhaust stack. No other units at the station use this stack.

The CT-121 is a second-generation FGD process and employs a unique absorber design, called a jet bubbling reactor (JBR), to combine conventional SO_2 absorption, neutralization, sulfite oxidation, and gypsum crystallization in one reaction vessel. The process is designed to operate in a pH range (3 to 5) where the driving force for limestone dissolution is high, resulting in nearly complete reagent utilization. Oxidation of sulfite to sulfate is also promoted at the lower pH because of the increased solubility of innate oxidation catalysts such as iron (Fe). Because all of the absorbed SO_2 is oxidized, there is sufficient surface area for gypsum crystal growth to prevent the slurry from becoming significantly supersaturated with calcium sulfate. This significantly reduces the potential for gypsum scaling, a problem

that frequently occurs in natural-oxidation FGD systems. Since much of the crystal attrition and secondary nucleation associated with the large centrifugal pumps in conventional FGD systems is also eliminated in the CT-121 design, large, easily dewatered gypsum crystals can be produced.

Flue gas from the boiler passes through the ESP and is pressurized by the Unit 1 ID fan. From the fan, the flue gas enters the gas-cooling section. Here, the flue gas is cooled and saturated with a mixture of JBR slurry, makeup water, and pond water. The quench slurry is sprayed into the gas at a liquid-to-gas ratio of about 10 gal/1000 acf at full boiler load using two centrifugal gas cooling pumps. The suction for the gas cooling pumps is located near the bottom of the JBR.

From the gas-cooling section, the flue gas enters the JBR. The JBR is the central feature of the CT-121 process. The gas enters an enclosed plenum chamber formed by an upper deck plate and a lower deck plate. Sparger tube openings in the lower deck plate force the gas into the slurry contained in the jet bubbling (froth) zone of the JBR vessel. After bubbling through the slurry, the gas flows upward through gas risers which pass through both the lower and upper deck plates. Entrained liquor in the gas disengages in a second plenum above the upper deck plate, and the cleaned gas passes to the mist eliminator.

The slurry in the JBR can be divided into two zones: the jet bubbling or froth zone and the reaction zone. SO_2 absorption occurs in the froth zone, while neutralization, sulfite oxidation, and crystal growth occur in both the froth and reaction zones.

The froth zone is formed when the untreated gas is accelerated through the sparger tubes in the lower deck and bubbled beneath the surface of the slurry at a depth of 6 to 16 inches. The froth zone provides the gas-liquid interfacial area for SO_2 mass transfer to

the slurry. The bubbles in the froth zone are continually collapsing and reforming to generate new and fresh interfacial area and to transport reaction products away from the froth zone to the reaction zone. The amount of interfacial area can be varied by changing the level in the JBR and, consequently, the injection depth of flue gas. The deeper the gas is injected into the slurry, the greater the interfacial area for mass transfer and the greater the SO_2 removal. In addition, at deeper sparger depths, there is an increase in the gas-phase residence time. SO_2 removal can also be increased by increasing the pH of the slurry in the froth zone. The pH is controlled by the amount of limestone fed to the reaction zone of the JBR.

The solids concentration in the JBR is maintained at a constant level by removing a slurry stream from the bottom of the reaction zone and pumping this stream to a holding tank (gypsum slurry transfer tank), where it is diluted with pond water before being pumped to the gypsum stack. This is done to keep the velocity high over a range of operating conditions.

The oxygen which reacts with absorbed SO_2 to produce sulfate is provided to some extent by oxygen diffusion from the flue gas, but the predominant source is air bubbled into the reaction zone of the JBR. The oxidation air lines enter through the very top of the JBR vessel, penetrate the upper and lower deck plates, and introduce the air near the bottom of the JBR. Oxygen diffuses from the air into the slurry as the bubbles rise to the froth zone of the JBR. Excess air mixes with the flue gas and exits the JBR to the mist eliminator. Before the oxidation air enters the JBR, it is saturated with service water to prevent a wet-dry interface at the discharge of the oxidation air lines.

Plant Yates uses an ash settling and storage area consisting of one ash-settling pond. Bottom ash from the boiler and pyrites from the pulverizers are sluiced together and are disposed of in the ash-

settling pond. The ESP ash, economizer ash, and air preheater ash are also sluiced together and disposed of in the same ash-settling pond. Water from the Chattahoochee River is used for cooling water in a once-through type steam condenser.

The ESP is a conventional weighted wire configuration typical of many of the older ESPs found on coal-fired utility boilers in the Midwest and Eastern parts of the United States. The specific collection area (SCA) is 210 ft^2/kacfm at full load.

The Plant Yates ESP uses a Forry Rapper Control System programmed to operate vibrators on the high voltage wire frames and electromechanical rappers on the collector plate assemblies. The rapping cycles are offset so that only one section of the plates is rapped at any single period of time. This rapping procedure results in smaller but more frequent spikes in opacity.

A Plant Yates process flow diagram is presented in Figure 3.8-1 and Figure 3.8-2 presents the trace element partitioning in the plant. Tables 3.8-1 and 3.8-2 present the trace element flow rates and concentration/removal efficiency information at key points in the power plant. Table 3.8-3 gives the stream temperatures at various points in the plant.

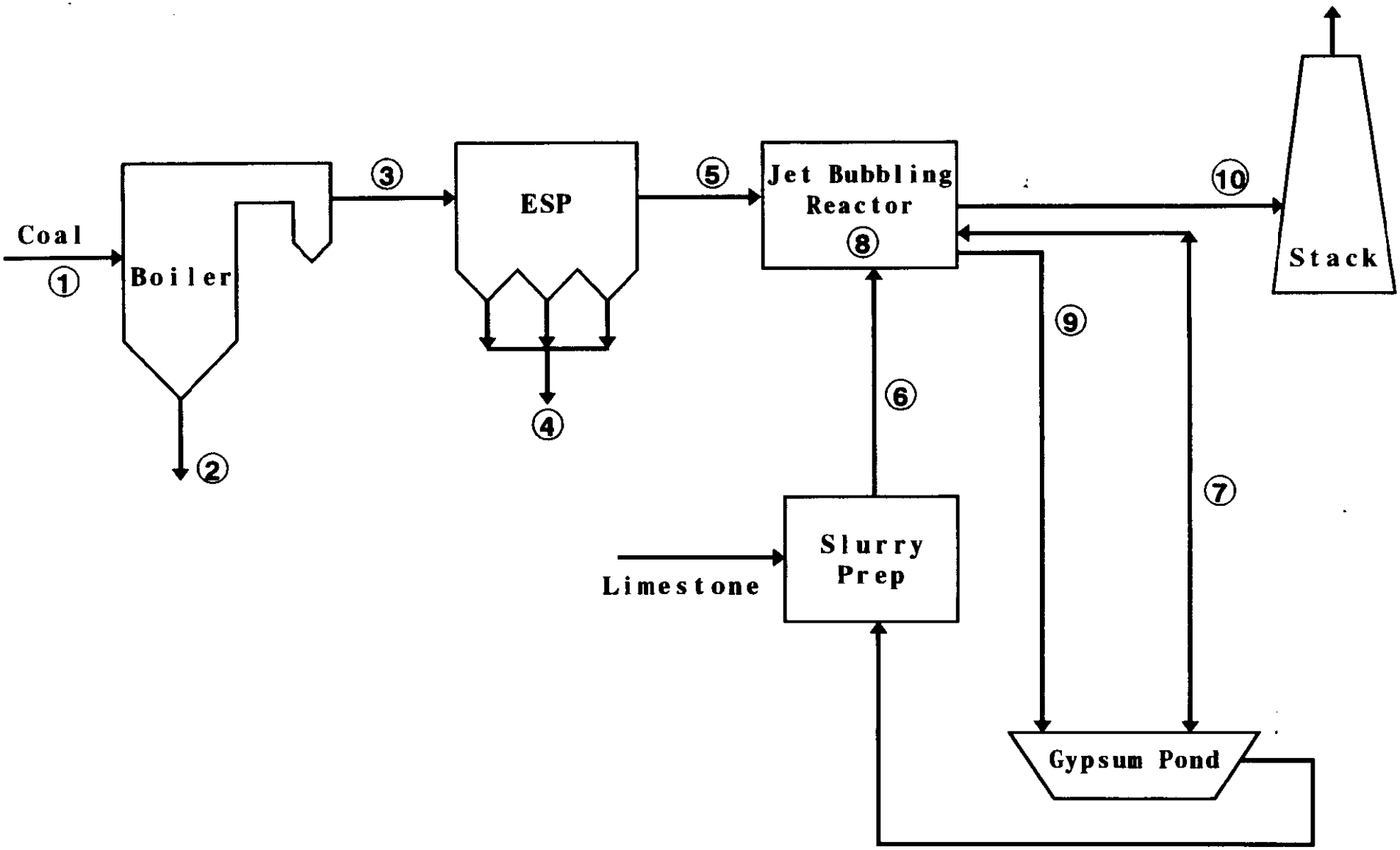

FIGURE 3.8-1. POWER PLANT YATES FLOW DIAGRAM

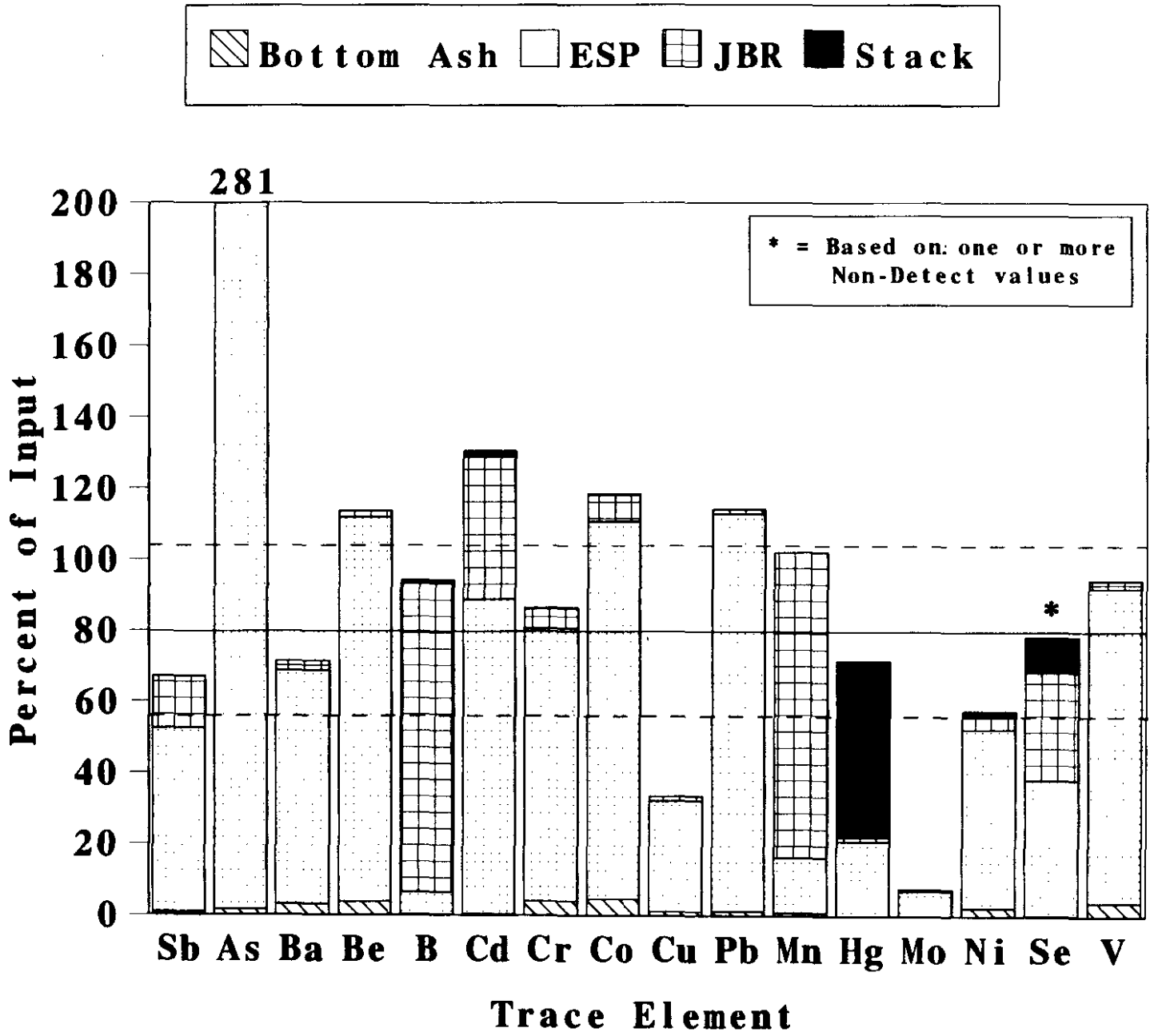

FIGURE 3.8-2. TRACE ELEMENTS IN OUTPUT STREAMS PLANT YATES

Table 3.8-1 Trace Element Flow Rates, Plant Yates

	(1) Coal In	(2) Bottom Ash	(3) Boiler Out, ESP In	(4) Collected Ash	(5) ESP Out, JBR In	(6) Limestone Reagent	(7) Recycle	(8) Accumu-lation	(9) JBR Blowdwn	(10) JBR Out, Stack
Units: lb/hr										
Antimony	0.049	0.0005	0.0327	0.0296	0.0004	0.0038[C]	ND< 0.0046 #	0.00006[C]	0.0084[C]	0.00006
Arsenic	0.184	0.0032	0.407	0.533	0.017	0.0038[C]	0.0080[C]	0.0002[C]	0.0116[C]	0.0012
Barium	6.42	0.20	4.37	4.33	0.074	0.10	0.077	0.0019	0.175	0.0029
Beryllium	0.0882	0.0034	0.0923	0.0969	0.0017	0.0013[A]	0.0002[A]	0.00004	0.0014	0.0001
Boron	8.02	0.123	6.5	4.10	6.85	23.0	33.9	0.438	56.4	0.442
Cadmium	0.0241	0.0001	0.0238	0.0358	0.0013	0.0053	0.0111	0.0002	0.0162	0.0006
Chromium	1.99	0.084	2.88	1.62	0.023	0.116	0.0047	0.0032	0.117	0.0054
Cobalt	0.281	0.014	0.274	0.322	0.0050	0.014	0.0090	0.0004	0.0227	0.0007[A]
Copper	2.89	0.0339	0.764	0.908	0.0169	0.0324	0.0034	0.0008	0.0350	0.0020
Lead	0.642	0.0088	0.704	0.725	0.0188	0.0084	0.0005[A]	0.0002	0.0086	0.0006
Manganese	1.88	0.119	2.10	2.14	0.034	4.29	7.72	0.099	11.9	0.0073
Mercury	0.0062	0.000005[B]	0.0129	0.0013	0.0057	0.00001[A]	0.00002	0.00005	0.00007	0.0031[A]
Molybdenum	1.79	0.0013[B]	0.317	0.122[A]	0.0086	0.0052	0.0059	0.0004	0.0107	0.0015
Nickel	2.41	0.0576	2.08	1.25	0.0238	0.0470	0.0398	0.0012	0.0856	0.0412
Selenium	0.184	ND< 0.0004 #	0.132	0.105	0.0794	0.0738	0.0170	0.0074[A]	0.0833[A]	0.0271
Vanadium	3.16	0.122	2.75	2.85	0.0546	0.0601	0.0141	0.0029	0.0713	0.0022

[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes three non-detect measurements
Non-detectible in all samples

Table 3.8-2 Concentrations and Removal Efficiencies, Plant Yates

	ESP Inlet, µg/Nm³	ESP Outlet JBR Inlet, µg/Nm³	JBR Outlet, µg/Nm³	ESP Removal Efficiencies, Percent	JBR Removal Efficiencies, Percent
Antimony	33	0.41	0.065	98.8	84.1
Arsenic	410	17	1.2	95.9	92.7
Barium	4,400	75	2.9	98.3	96.1
Beryllium	93	1.7	0.099	98.1	92.6
Boron	6,600	6,900	440	34.3	93.5
Cadmium	24	1.3	0.63	95.1	46.2
Chromium	2,900	23	5.4	98.7	76.6
Cobalt	276	5	0.74	98.2	85.3
Copper	770	17	2.0	97.8	88.1
Lead	710	19	0.61	97.4	96.7
Manganese	2,120	34	7.3	98.4	78.4
Mercury	13	5.7	3.1	16.5	45.9
Molybdenum	320	8.7	1.5	97.2	82.5
Nickel	2,100	24	41	98.8	-75.5
Selenium	133	80	27	38.1	66.9
Vanadium	2,770	55	2.2	98	96

Table 3.8-3 Stream Temperatures, Plant Yates

Temperature, deg F	
ESP Inlet	304
ESP Outlet	280
JBR Scrubber	---
Stack	129

Section 3.9 Bailly Station

The Bailly Generating Station is owned and operated by the Northern Indiana Public Service Company (NIPSCO). The plant is located on the shores of Lake Michigan near Chesterton, Indiana. This project involved the two coal-fired units of the Bailly Generating Station with a combined capacity of 528 MWe; Unit No. 7 has a gross capacity of 183 MWe and Unit No. 8 has a gross capacity of 345 MWe.

Each unit is equipped with a Babcock & Wilcox cyclone boiler and a steam turbine generator. Both units burn an Illinois/Indiana basin high-sulfur bituminous coal (2.5% to 4.5% sulfur). Unit 7 has four cyclone burners, and Unit 8 has eight cyclone burners. Full load on each unit usually varies by ± 3MW. There is no control technology for NO_x emissions.

Electrostatic precipitators (ESPs) are used on both units for particulate control. There are two ESPs on Unit 8 and one ESP on Unit 7. The two ESPs of Unit No. 8 are identical to the Unit No. 7 ESP. Each ESP is two shells wide and has 12 electrical fields. In addition, there are three rows of hoppers to collect fly ash from the 12 fields of each ESP. Thus, there are three hoppers in the direction of gas flow along any given lane of the ESP.

Ammonia is injected at a rate to yield 15 ppm concentration prior to the Unit No. 7 ESP and prior to each of the two Unit No. 8 ESPs for the control of SO_3 to prevent acid mist emissions. There are separate ammonia injection systems for the two units.

The Bailly Station Unit No. 7 flue gas flows through a single duct into the ESP. The flue gas stream exits the ESP and subsequently connects downstream of the ESP with the flue gas duct from the combined outlets of the two ESPs of Unit No. 8. These two flue gas streams then join to form a single stream.

There are various ash disposal systems for Units No. 7 and No. 8 at the Bailly Station. Based on four years of records of waste disposal from the plant, nominally 63% of the ash in the coal is collected as bottom ash and the remaining 37% is fly ash. Wet bottom ash is transferred to a slag tank where the ash is sluiced to an ash settling pond. The slag tank is dumped every six hours. The water from the settling pond is recycled back for the sluicing of the bottom ash. Economizer ash is not accumulated or evacuated in sufficient quantity or frequency to be considered as a separate waste stream. Makeup water is obtained from on-site facilities. Fly ash from the precipitators from both units is conveyed dry to an ash silo where it is trucked away to a landfill or sold.

Both units use Lake Michigan water as a once-through cooling medium.

Sulfur dioxide in the combined flue gas stream from the two units of the Bailly Generating Station is treated by the Advanced Flue Gas Desulfurization (AFGD) demonstration project managed by Pure Air of Allentown, Pennsylvania, (a joint venture of Air Products, Inc. and Mitsubishi Heavy Industries, Ltd.) under the Department of Energy's Clean Coal Technology program. The scrubber is owned and operated by Pure Air on the Lake. Pure Air's AFGD system is using wet limestone flue gas desulfurization (FGD) technology to achieve a high level of SO_2 removal (90 to 95+ percent capability) on high sulfur U.S. coals.

A feature of the AFGD process is the purchase and direct injection of powdered limestone in lieu of on-site limestone milling operations. This project includes an in-situ oxidation absorber module that produces high-quality gypsum from a range of high sulfur coals. These features serve to decrease facility size and costs for both installation and operation of the process. High-quality, by-product gypsum (93+ percent purity) is being produced and sold to a wallboard manufacturer. This by-product utilization

eliminates the problem of solid waste disposal and also contributes to the cost-effectiveness of the technology.

The flue gas stream from the AFGD process is vented to the atmosphere through a 480-foot stack.

Figure 3.9-1 is a flow diagram of Bailly Station Units 7 and 8. Figure 3.9-2 presents the trace element partitioning. Tables 3.9-1 and 3.9-2 comprise the trace element flow rates and concentration/removal efficiency results. Table 3.9-3 gives stream temperatures at various points in the plant.

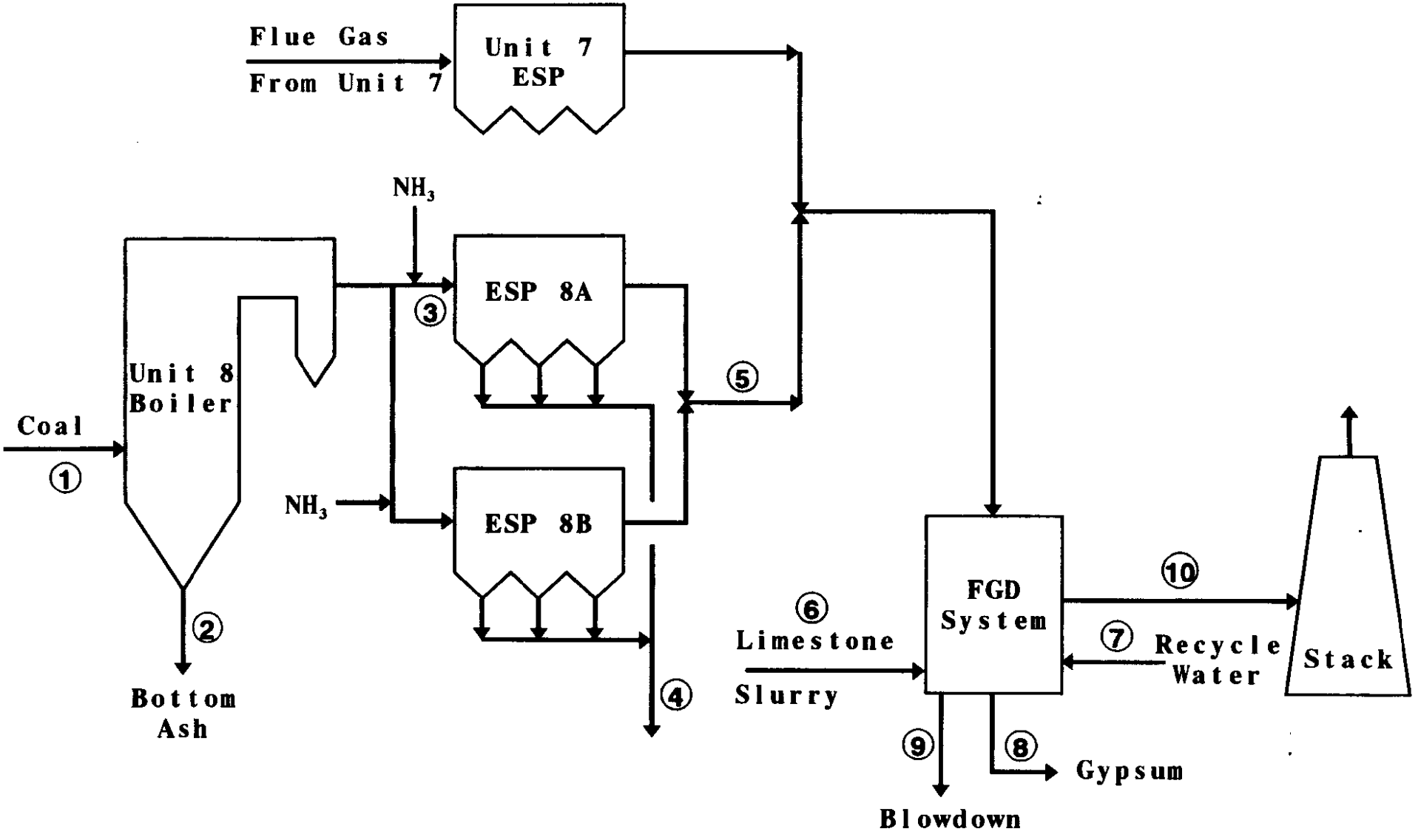

FIGURE 3.9-1. UNIT 7 & 8 FLOW DIAGRAM - BAILLY GENERATING STATION

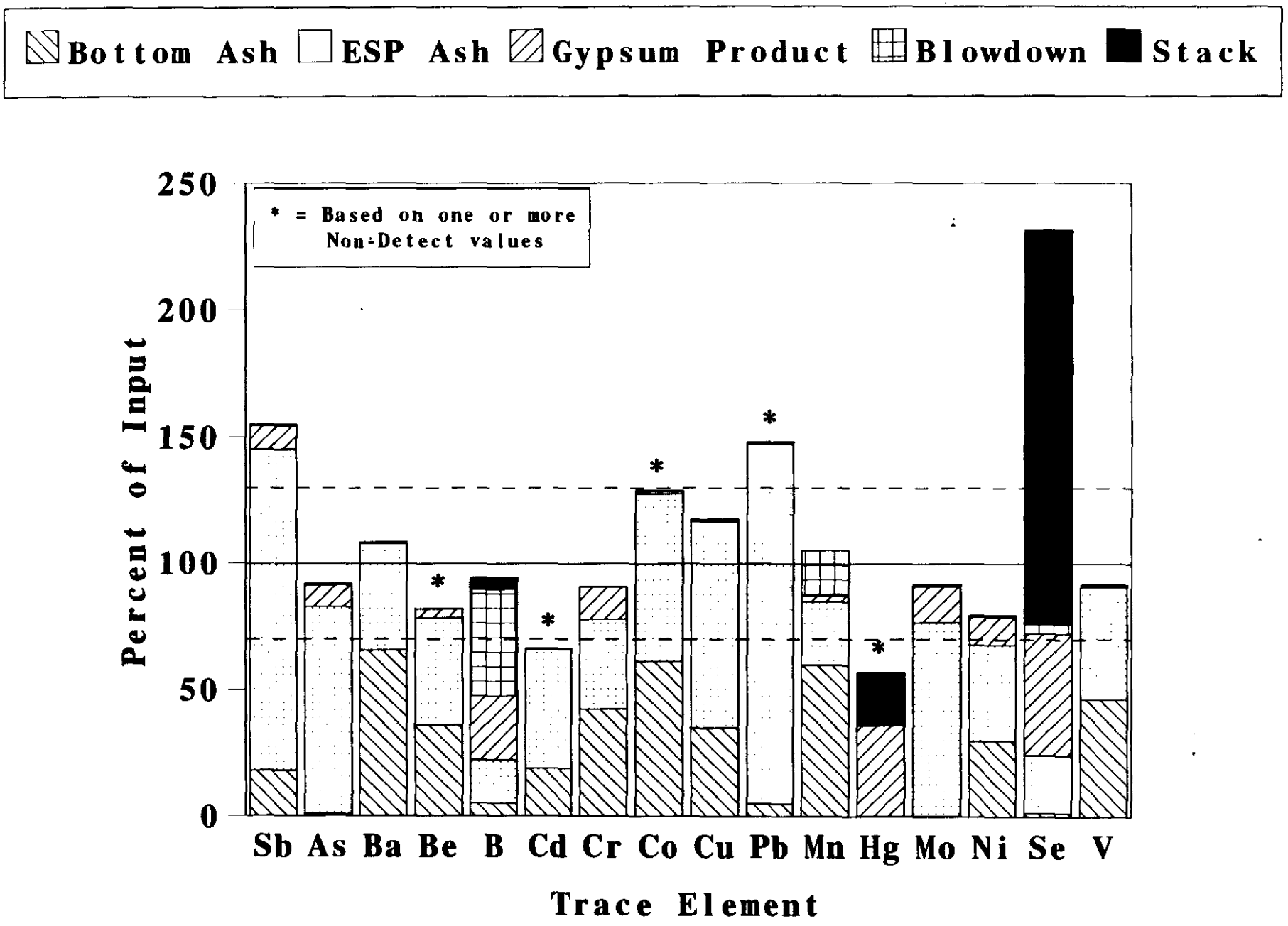

FIGURE 3.9-2. TRACE ELEMENTS IN OUTPUT STREAMS BAILLY STATION

Table 3.9-1 Trace Element Flow Rates, Bailly Station

	(1) Coal	(2) Bottom Ash	(3) ESP B Inlet	(4) ESP B Hopper Ash	(5) Scrubber In (ESP B Only)	(6) Lime Reagent	(7) Scrubber/ Makeup Water	(8) Scrubber Gypsum	(9) Scrubber Blowdown	(10) Stack
Units: lb/hr										
Antimony	0.200	0.042	0.091	0.298	0.00059	0.035	ND< 0.00013 #	0.022	0.00030	0.00094
Arsenic	0.873	0.0076	0.551	0.721	0.0051	0.010	ND< 0.00007 #	0.077	0.00055	0.0050
Barium	13.0	8.57	4.13	5.49	0.0139	0.048	0.0081	0.056	0.0100	0.0044
Beryllium	0.534	0.191	0.213	0.226	0.00020[A]	ND< 0.00014 #	ND< 0.00011 #	0.019	ND< 0.00001 #	ND< 0.00026[A]
Boron	62.5	3.35	37.5	11.5	33.2	4.55	ND< 0.0140 #	16.9	28.4	3.01
Cadmium	0.825	0.156	0.349	0.389	0.0094	ND< 0.0012[B]	0.00055	ND< 0.00047 #	0.0018	0.0014
Chromium	13.0	5.49	4.44	4.63	0.0190	0.021	ND< 0.0013 #	1.67	0.00023	0.0091
Cobalt	0.779	0.483	0.412	0.522	0.00061	0.010	0.00085	ND< 0.0070 #	0.0039	0.00036
Copper	2.93	1.05	2.05	2.45	0.0083	0.080	0.0024	0.020	0.00041	0.0057
Lead	2.37	0.121	3.11	3.37	0.0111	ND< 0.0022 #	ND< 0.0011 #	ND< 0.012 #	ND< 0.00012 #	0.0053
Manganese	8.97	6.83	2.56	2.82	0.0032	2.44	0.0023	0.284	2.05	0.0077
Mercury	0.032	ND< 0.00003[B]	0.0090	0.0001	0.0098	ND< 0.00004 #	0.00004	0.012	0.00002	0.0068
Molybdenum	2.25	0.0089[B]	1.63	1.72	0.0117	0.013	0.0109	0.320	0.0058	0.0113
Nickel	7.19	2.17	2.63	2.77	0.0153	0.090	0.0023	0.807	0.0354	0.0067
Selenium	0.407	0.0065	0.873	0.093	0.418	ND< 0.0018 #	0.00056	0.196	0.0148	0.636
Vanadium	14.8	6.90	5.56	6.61	0.0099	0.127	ND< 0.00067 #	0.099	0.00058	0.0091

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.9-2 Concentrations and Removal Efficiencies, Bailly Station

	ESP-8 Inlet, µg/Nm³	ESP-8 Outlet, µg/Nm³	ESP-7 Outlet, µg/Nm³	Scrubber Inlet, µg/Nm³	Stack, µg/Nm³	ESP-8 Removal Efficiencies, Percent	ESP-7 Removal Efficiencies, Percent	Scrubber Removal Efficiencies, Percent
Antimony	43	0.235	0.416	0.310	0.38	99.97	98.83	-57.5
Arsenic	132	2.1	6.4	3.65	1.43	98.41	95.05	58.26
Barium	1,920	5.66	23.7	12.1	1.71	99.7	98.75	89.18
Beryllium	99	ND< 0.09	1.38	0.542	ND< 0.10	99.92	98.58	88.7
Boron	17,400	13,600	13,300	13,481	1,230	19.43	20.8	91.16
Cadmium	163	3.81	9.45	5.82	0.57	97.33	93.78	90.15
Chromium	2,080	7.75	35.4	14.9	3.7	100.14	98.97	60.98
Cobalt	191	0.158	2.18	0.903	ND< 0.10	99.62	98.29	79.3
Copper	958	3.4	15.1	7.51	2.33	99.64	98.36	70.11
Lead	1,440	4.57	23.4	11.2	2.13	99.68	98.34	82.35
Manganese	1,200	1.73	10.7	4.05	4.16	99.85	99.22	62.45
Mercury	4.2	4.02	4.21	4.09	2.8	-5.10	8.22	52.68
Molybdenum	760	4.57	16.9	9.05	4.61	99.38	97.72	49.92
Nickel	1,240	6.5	17	6.92	2.92	99.45	98.63	70.34
Selenium	408	171	347	232	261	57.73	11.71	-15.68
Vanadium	2,590	4.32	38.2	16.0	3.81	99.83	98.49	76.92

Table 3.9-3 Stream Temperatures, Bailly Station

Temperature, deg F	
Unit 7	
Economizer Inlet	815
Steam, as throttle	655
ESP Outlet	296
Unit 8	
Economizer Inlet	942
Economizer Outlet	613
ESP Outlet	313
AFGD Inlet	319
AFGD Outlet	131

Section 3.10 Nelson Dewey Station

Plant Description

The site for this test was Unit 2 of the Nelson Dewey Station, which is owned and operated by Wisconsin Power and Light. This unit is equipped with three cyclone burners and is a forced draft unit with a nominal capacity of 100 MWe. The test unit burns an Indiana bituminous coal.

Environmental controls consist of an ESP for particulate control and a coal-fired reburn system for NO_x control. The reburn system was recently retrofitted to this unit and consists of the pulverizer, reburn burners in the upper furnace, overfire air ports, and modifications to the control system. The unit could be operated in either the baseline mode without the reburn burners or in the low-NO_x mode with approximately 20 percent of the heat input from the reburn burners. Under low NO_x reburn operation, the existing cyclone burners are fired with 70 to 80 percent of the total coal feed as crushed coal. The cyclones are operated at around 110 percent excess air in the main combustion zone. The reburn burners are fired with the remaining 20 to 30 percent of the coal feed as pulverized coal. These reburn burners are operated fuel rich at a reducing stoichiometry of 0.85 to 0.95. This reducing condition converts the nitrogen oxides formed in the cyclone burners to molecular nitrogen, thereby reducing NO_x. The balance of air required to complete combustion is added in the burnout zone above the reburn zone through the use of overfire air ports.

The standard baseline coal which was used throughout the development of the reburn system was a bituminous Indiana Lamar coal with a heating value of about 11,500 Btu/lb, a sulfur level of about 1.6 percent, and ash content of about 9 percent. The plant was converting to subbituminous western coal as the standard fuel

after the test. As a result, the remaining supply of Lamar coal was very limited and the plant totally consumed the residual Lamar supply during the HAP testing. Some decisions on test priorities, sequencing, and duration of runs were structured around the need to stretch out the coal supply. To conserve coal, the unit was normally operated at low load between tests. During testing, and 2 hours before, the unit was operated at full load. At other times, however, the unit was fired at the lowest practical load to conserve remaining coal and maximize the flexibility for test run times.

Figure 3.10-1 shows a schematic flow diagram of the test unit. Figures 3.10-2 and 3.10-3 show trace element partitioning results during baseline operation and during reburn testing. Tables 3.10-1 and 3.10-2 present the trace element flow rates during these two periods. Table 3.10-3 gives trace element concentrations and removal efficiencies for both periods. Table 3.10-4 gives stream temperatures at various points in the plant.

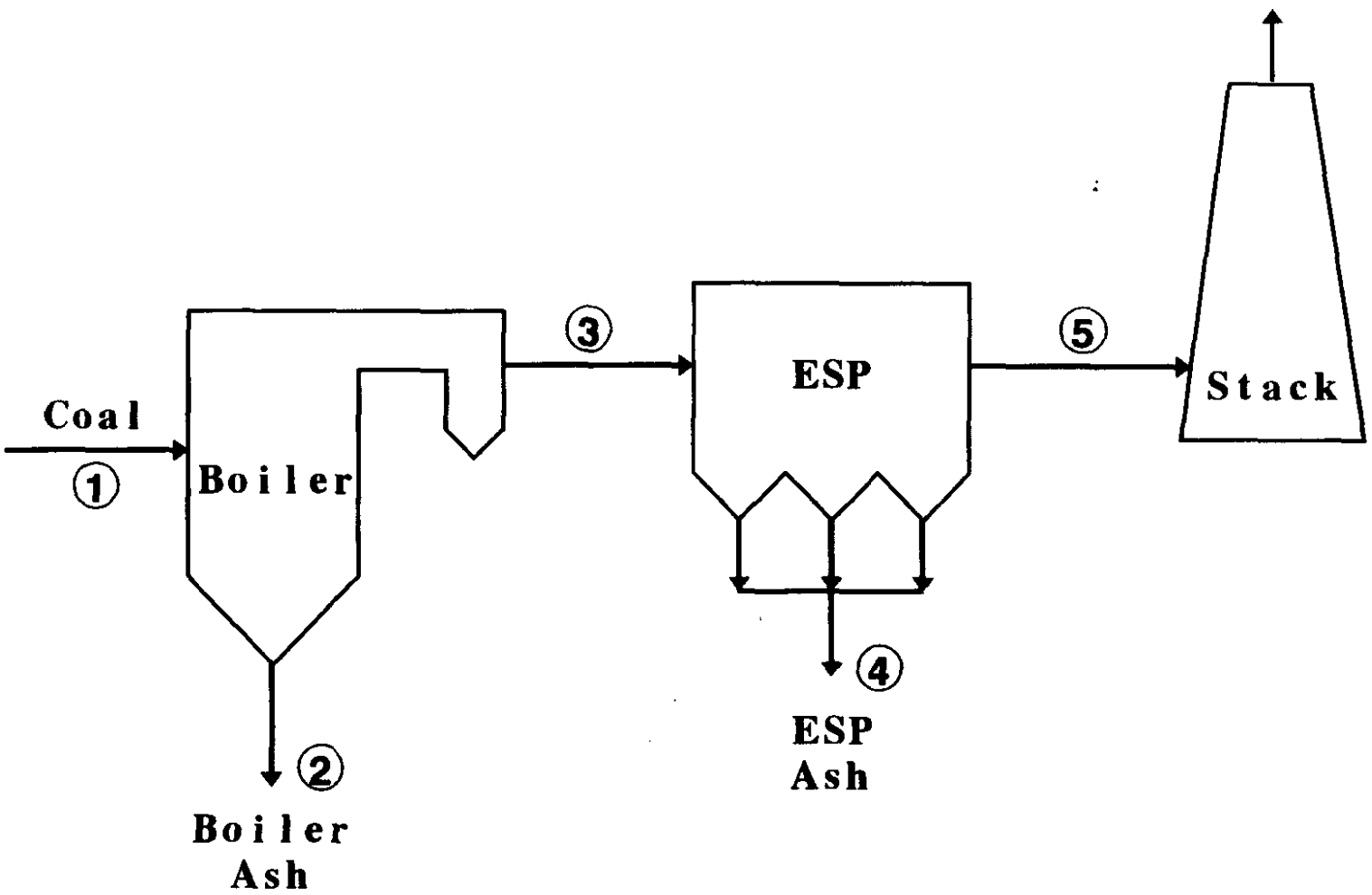

FIGURE 3.10-1. NELSON DEWEY STATION

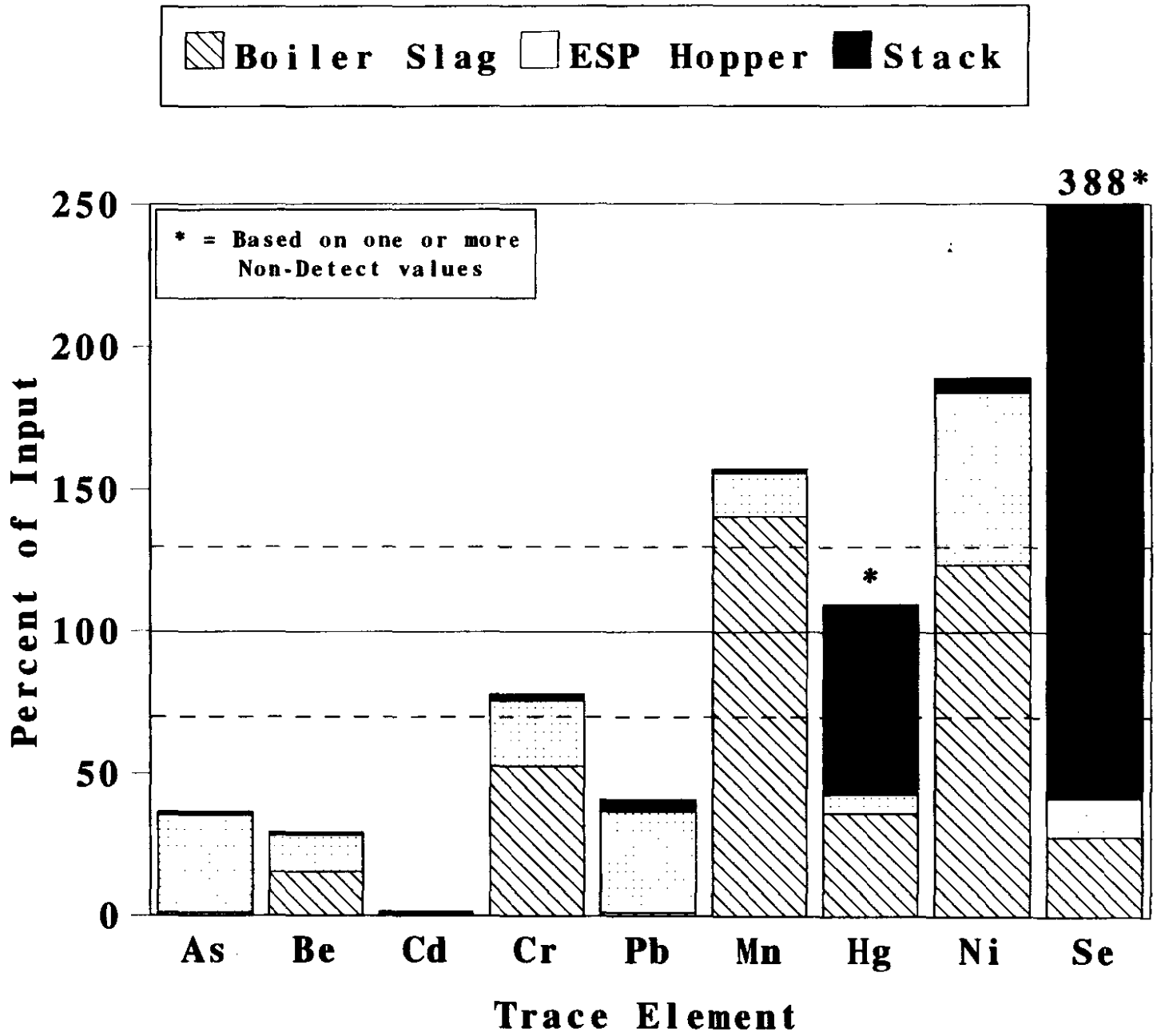

FIGURE 3.10-2. TRACE ELEMENTS IN OUTPUT STREAMS NELSON DEWEY STATION, BASELINE TESTS

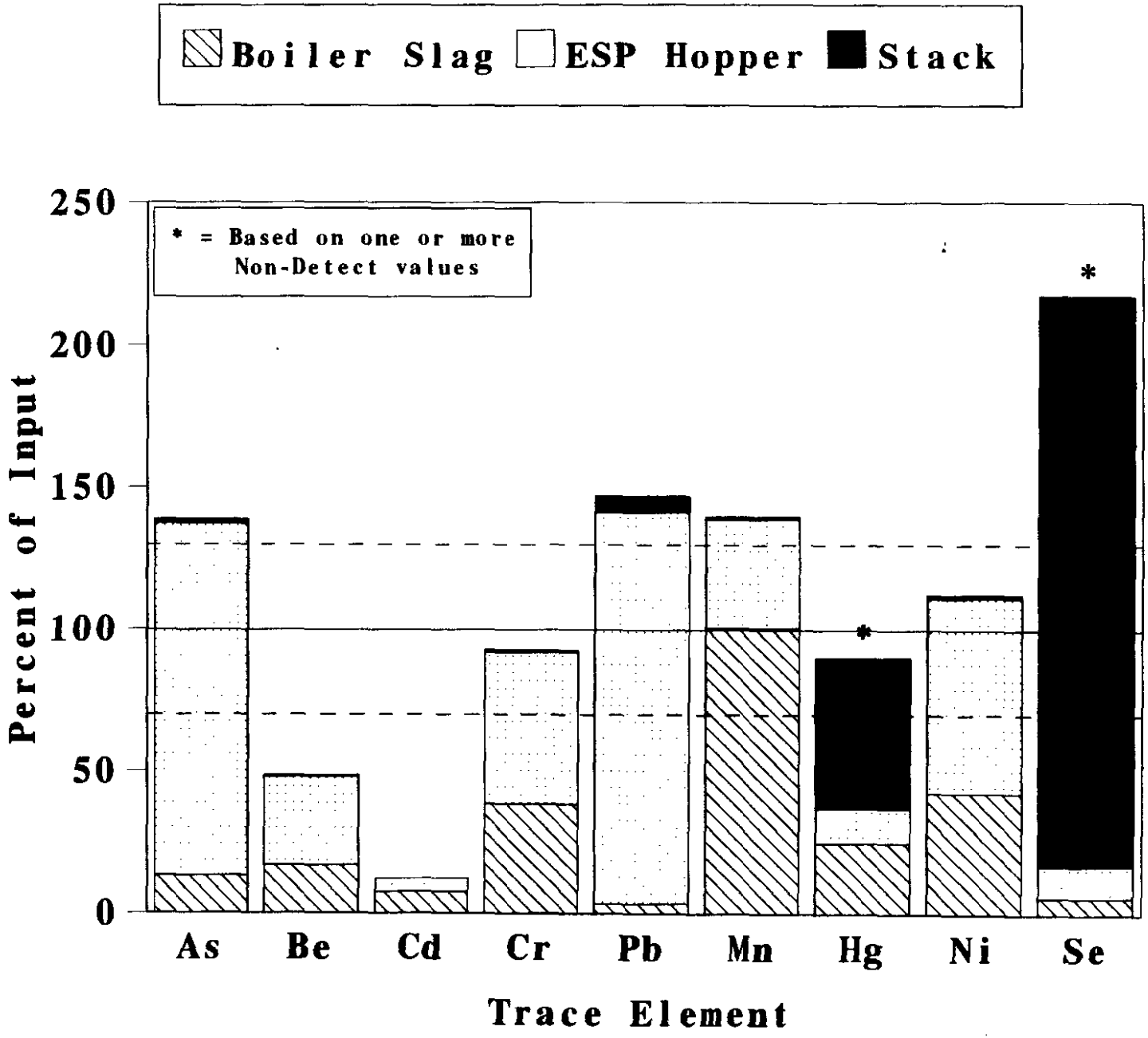

FIGURE 3.10-3. TRACE ELEMENTS IN OUTPUT STREAMS NELSON DEWEY STATION, REBURN TESTS

Table 3.10-1 Trace Element Flow Rates, Nelson Dewey Station, Baseline Data

	(1) Coal Input	(2) Boiler Slag	(3) ESP Inlet	(4) ESP Ash	(5) Stack
Units: lb/hr					
Arsenic	0.955	0.0106[B]	0.188	0.326	0.0103
Beryllium	0.286	0.044	0.056	0.037	0.0032
Cadmium	3.0[A]	0.025	0.030	0.0156[A]	0.0037
Chromium	0.892	0.468	0.338	0.206	0.019
Lead	2.88	0.037[A]	1.91	1.02	0.121
Manganese	2.09	2.94	0.543	0.318	0.029
Mercury	ND< 0.0095 #	ND< 0.0034 #	0.010	ND< 0.00063 #	0.0063
Nickel	2.14	2.65	1.91	1.30	0.107
Selenium	ND< 0.095 #	0.0265[B]	0.0331	ND< 0.013 #	0.330

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
\# Non-detectible in all samples

Table 3.10-2 Trace Element Flow Rates, Nelson Dewey Station, Reburn Data

	(1) Coal	(2) Slag	(3) ESP in	(4) Hopper Ash	(5) ESP out, Stack
Units: lb/hr					
Arsenic	0.672	0.088[B]	0.198	0.833	0.011
Beryllium	0.275	0.047[A]	0.047	0.085	0.0013
Cadmium	3.95[A]	0.300[A]	0.033	0.179[B]	0.0021
Chromium	0.791	0.304	0.212	0.421	0.0066
Lead	1.30	0.046	1.29	1.78	0.075
Manganese	2.26	2.28	0.484	0.865	0.021
Mercury	ND< 0.0095 #	ND< 0.0024 #	0.0066	0.0012[B]	0.0050
Nickel	3.86	1.64	0.543	2.65	0.044
Selenium	ND< 0.095 #	ND< 0.0056 #	0.132	0.011[A]	0.191

ND< Value shown is detection limit.
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
\# Non-detectible in all samples

Table 3.10-3 Concentrations and Removal Efficiencies, Nelson Dewey Station

	Baseline			Reburn		
	ESP In, µg/dscm	ESP Out, µg/dscm	Removal Efficiencies, Percent	ESP In, µg/dscm	ESP Out, µg/dscm	Removal Efficiencies, Percent
Arsenic	196	11.0	94.4	218	12.1	94.5
Beryllium	57.0	3.61	93.7	52.1	1.31	97.5
Cadmium	30.9	3.98	87.1	36.4	2.37	93.5
Chromium	347	20.5	94.1	234	7.40	96.8
Lead	1,953	127	93.5	1,426	78.0	94.5
Manganese	560	31.2	94.4	535	23.1	95.7
Mercury	10.2	6.87	32.7	7.45	5.66	24.0
Nickel	2,034	117	94.3	599	49.7	91.7
Selenium	34.9	357	--	146	218	--

Table 3.10-4 Stream Temperatures, Nelson Dewey Station

Temperature, deg F	
ESP Inlet	513
Stack	492

Section 3.11 Plant Hammond

Plant Description

The unit tested, Plant Hammond, has a generating capacity of approximately 500 MWe. The opposed wall-fired, subcritical boiler was designed by Foster Wheeler. A partial vertical dividing plate within the furnace creates two combustion zones, and very little mixing of the flue gas occurs between the A and B sides.

The plant burns a combination of bituminous coals that have a typical sulfur content of 1.6% and a typical ash content of 10%. Bottom ash is removed from the boiler by an ash sluicing system. Electrostatic precipitators (ESPs) remove fly ash from the flue gases. The flue gas treatment and ash removal facilities are described in greater detail below.

The flue gas exiting each side of the furnace flows into a separate duct, designated the A or B side. Two ESPs, one each for the A and B sides, remove particulate matter from the flue gas. The unit is equipped with a conditioning system capable of injecting SO_3 or NH_3 into the flue gas upstream of the ESPs to improve ESP performance. The conditioning system was not in use during the Over-Fire Air (OFA) testing. During the Over-Fire Air/Low NO_x Burner (OFA/LNB) test, NH_3 was injected at a rate of approximately 25 scfm, which is equivalent to a concentration of about 20 ppmv in the flue gas entering the ESPs. The NH_3 injection was used because of plant concerns about complying with particulate matter emission limits.

Dry ash collected in the economizer and ESP hoppers is pneumatically transported to a tank where it is mixed with water and sluiced to a settling pond. Bottom ash from the boiler is sluiced to a separate settling pond. The water used for ash sluicing is recycled water from the settling ponds.

Overfire air ports were installed during a four-week outage in the spring of 1990 by Foster Wheeler Energy Corporation (FWEC). The design includes four overfire air ports on each side of the boiler directly above the top row of burners. Overfire air is diverted from the secondary air ductwork. At full load, approximately 20% of the secondary air is introduced through the overfire air ports.

The low-NO_x burners were installed during a seven-week outage in the spring of 1991. The FWEC burners are of the controlled flow/split flame (CFSF) design. The 24 burners are arranged on opposing walls, with three rows of four burners on each wall. The low-NO_x burners replaced the previous pre-NSPS Intervane burners that were in place during the OFA test.

The Plant Hammond flow diagram is shown in Figure 3.11-1. Partitioning results for the two test periods are given in Figure 3.11-2 and 3.11-3. Tables 3.11-1 and 3.11-2 present trace element flow rates for both (overfire air and low-NO_x burner) test periods. Table 3.11-3 shows trace element concentrations and removal efficiency data for both test periods. Table 3.11-4 gives stream temperatures at various points in the plant.

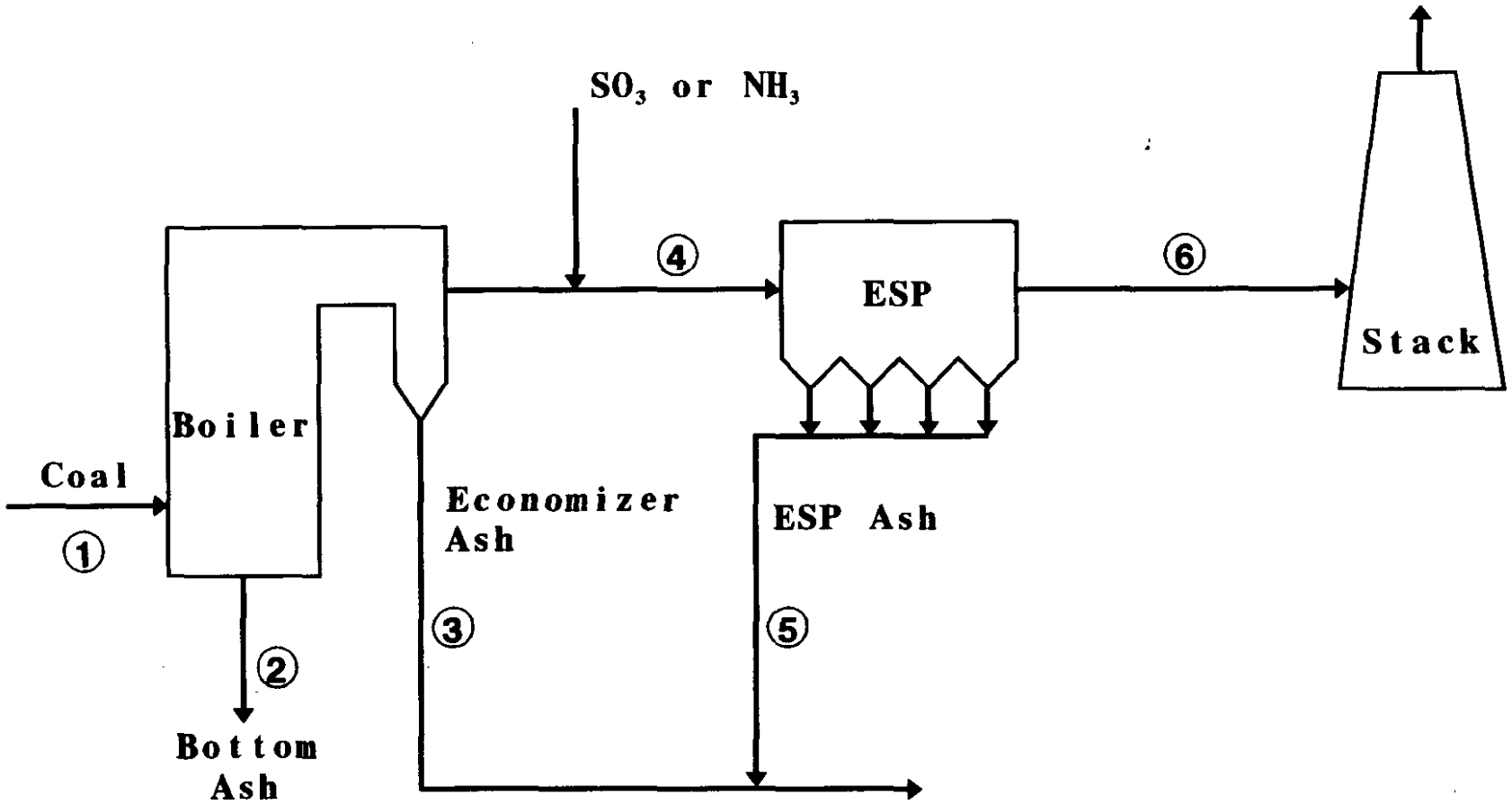

FIGURE 3.11-1. PLANT HAMMOND FLOW DIAGRAM

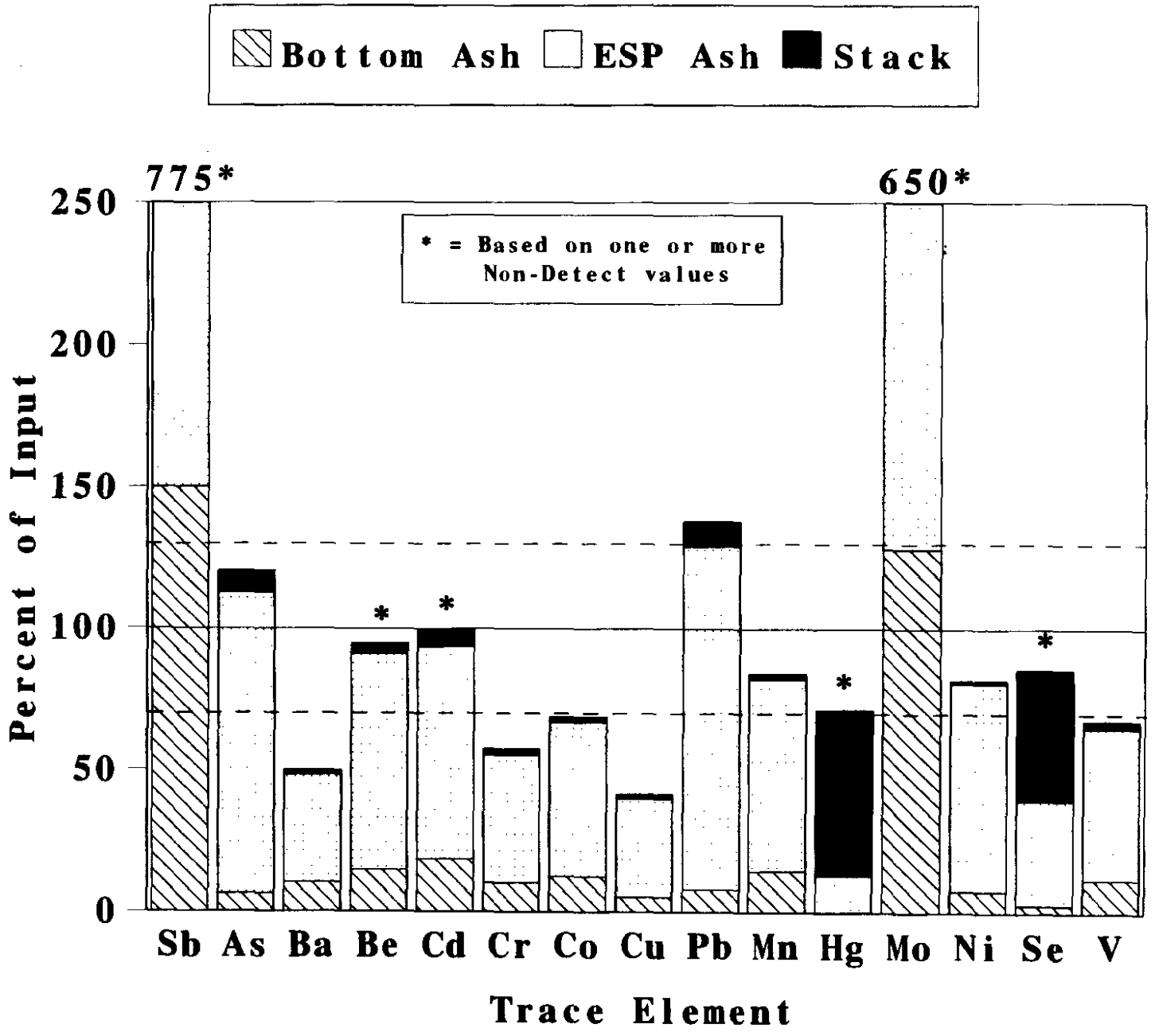

FIGURE 3.11-2. TRACE ELEMENTS IN OUTPUT STREAMS PLANT HAMMOND, OVER FIRE AIR

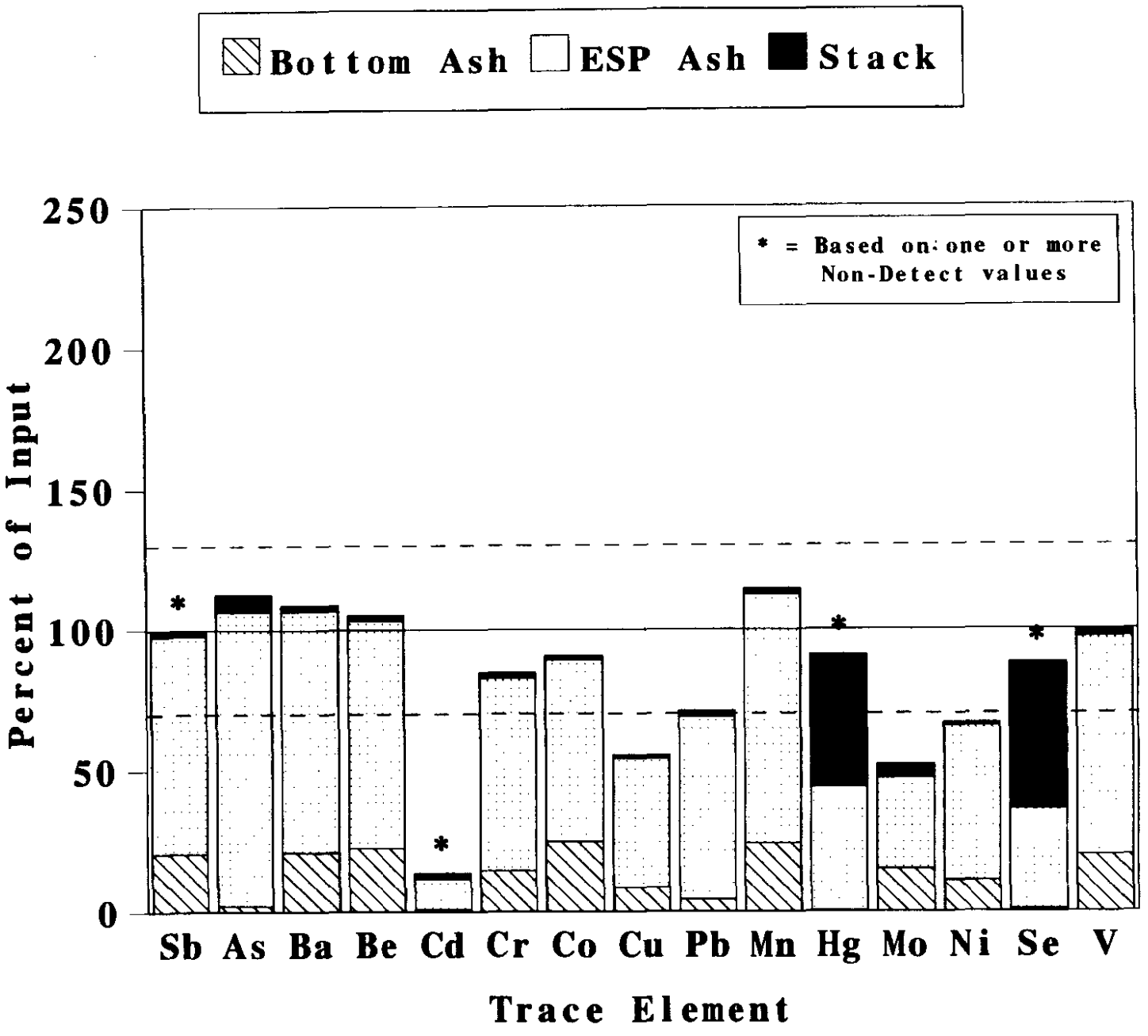

FIGURE 3.11-3. TRACE ELEMENTS IN OUTPUT STREAMS PLANT HAMMOND, LOW NOx BURNER

Table 3.11-1 Trace Element Flow Rates, Plant Hammond, Over-Fire Air Tests

	(1) Coal	(2) Bottom Ash	(3) ESP Inlet	(4) ESP Ash	(5) Stack
Units: lb/hr					
Antimony	0.452	ND< 0.677 #	ND< 2.65 #	ND< 2.71 #	ND< 0.122 #
Arsenic	5.61	0.352	8.10	5.96	0.424
Barium	56.1	5.82	28.3	21.1	1.00
Beryllium	0.462	0.0677	0.490	0.352	ND< 0.0166 #
Cadmium	0.0363[B]	ND< 0.0068 #	0.0495[A]	ND< 0.0271 #	ND< 0.0023 #
Chromium	7.26	0.745	4.23	3.25	0.170
Cobalt	2.74	0.339	1.66	1.49	0.0502
Copper	12.5	0.657	5.40	4.34	0.185
Lead	1.68	0.135	1.98	2.03	0.150
Manganese	5.61	0.812	3.37	3.79	0.112
Mercury	0.0495	ND< 0.00014 #	0.0319	0.0062	0.0289
Molybdenum	1.06[A]	ND< 1.35 #	ND< 1.304 #	5.42	0.054[C]
Nickel	8.91	0.677	2.97	6.50	0.108
Selenium	1.25	ND< 0.0339 #	2.11	0.461	0.579
Vanadium	12.2	1.42	8.10	6.50	0.324

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Non-detectible in all but one sample
\# Non-detectible in all samples

Table 3.11-2 Trace Element Flow Rates, Plant Hammond, Low-NO_x Burner Tests

	(1) Coal	(2) Bottom Ash	(3) ESP Inlet	(4) ESP Ash	(5) Stack
Units: lb/hr					
Antimony	0.47	0.097[B]	ND< 0.38 #	ND< 0.36 #	0.010
Arsenic	7.25	0.162	7.86	7.53	0.452
Barium	31.2	6.50	26.2	26.7	0.603
Beryllium	0.693	0.155	0.567	0.559	0.013
Cadmium	ND< 0.819 #	ND< 0.0071 #	0.092	0.087	0.016
Chromium	5.36	0.777	3.67	3.65	0.114
Cobalt	1.92	0.473	1.27	1.24	0.028
Copper	10.7	0.918	4.80	4.86	0.132
Lead	2.30	0.099	1.48	1.48	0.049
Manganese	4.41	1.06	3.88	3.89	0.090
Mercury	0.044	ND< 0.0001 #	0.048	0.019	0.021
Molybdenum	1.13[A]	0.169[A]	0.375[A]	0.365	0.053
Nickel	5.36	0.579	2.88	2.92	0.072
Selenium	1.17	ND< 0.0085 #	0.432	0.413	0.603
Vanadium	8.19	1.62	6.55	6.32	0.177

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.11-3 Concentrations and Removal Efficiencies, Plant Hammond

	Over Fire Air Tests			Low NOx Burner Tests		
	ESP Inlet, $\mu g/Nm^3$	Stack, $\mu g/Nm^3$	OFA Removal Efficiencies, Percent	ESP Inlet, $\mu g/Nm^3$	Stack, $\mu g/Nm^3$	OFA/LNB Removal Efficiencies, Percent
Antimony	ND< 590	ND< 29	NC	ND< 87	2.6	NC
Arsenic	1,800	110	95	1,800	120	94
Barium	6,300	260	96	6,000	160	98
Beryllium	109	4.3	97	130	3.5	98
Boron						
Cadmium	ND< 11	0.59	NC	21	4.2	83
Chromium	940	44	96	840	24.	98
Cobalt	370	13	97	290	7.5	98
Copper	1,200	48	97	1,100	35	98
Lead	440	39	92	340	13	97
Manganese	750	29	97	890	24	98
Mercury	7.1	7.5	9	11	5.5	55
Molybdenum	ND< 290	ND< 14	NC	86	14	86
Nickel	660	28	96	660	19	98
Selenium	470	150	72	99	160	0
Vanadium	1,800	84	96	1,500	47	97

NC = Not Calculated.

Table 3.11-4 Stream Temperatures, Plant Hammond

Temperature, deg F	
ESP Inlet	303
ESP Outlet (To Stack)	305

Section 3.12 Plant Smith

Plant Description

There are two units at Plant Smith. Unit 1 is rated at 175 MWe and Unit 2, the test unit, at 196 MWe. Both units have tangentially-fired boilers. Originally, both units were equipped with cold-side ESPs; in 1977, however, when the units were converted to balanced draft operation, both units were also retrofitted with hot-side ESPs. Both units continue to operate with a hot-side and a cold-side ESP in tandem. Flue gas leaving the two cold-side ESPs is vented to the atmosphere through a common stack.

Over the years, the fuel supply at the test site has varied. About 10 years ago, for example, a low-sulfur coal from South Africa was employed. During the past year or longer, on the other hand, coals from Southern Illinois and Western Kentucky containing about 3% sulfur have been used as the fuel. A 3% sulfur Western Kentucky coal, purchased on the spot market was burned during both of the test occasions described in this report. There is no provision at the test site for the removal of sulfur from the flue gas in a scrubber of any type; however, a portion of the sulfur present in the coal as pyrite is removed during the pulverization process prior to combustion and is discharged as a waste stream.

During the first half of 1991, the furnace of Unit 2 began to undergo modification with the installation of low NO_x burners. This report includes the measurement of rates of toxic organic and inorganic substances in the flue gas both before and after the burner modifications were made. The measurements prior to the final adoption of modified combustion conditions were conducted during the period September 17-22, 1991; however, the baseline study was performed after certain structural changes in the furnace had been completed. The subsequent measurements with burner

modifications in place were made during the period January 14-17, 1992.

Figure 3.12-1 shows the flow arrangement for Plant Smith. Figures 3.12-2 and 3.12-3 give partitioning results for baseline and Low-NO_x test periods. Trace element flow rates are given for both periods in Tables 3.12-1 and 3.12-2. Table 3.12-3 gives concentrations and removal efficiencies for trace elements during both periods. Table 3.12-4 gives stream temperatures at various points in the plant.

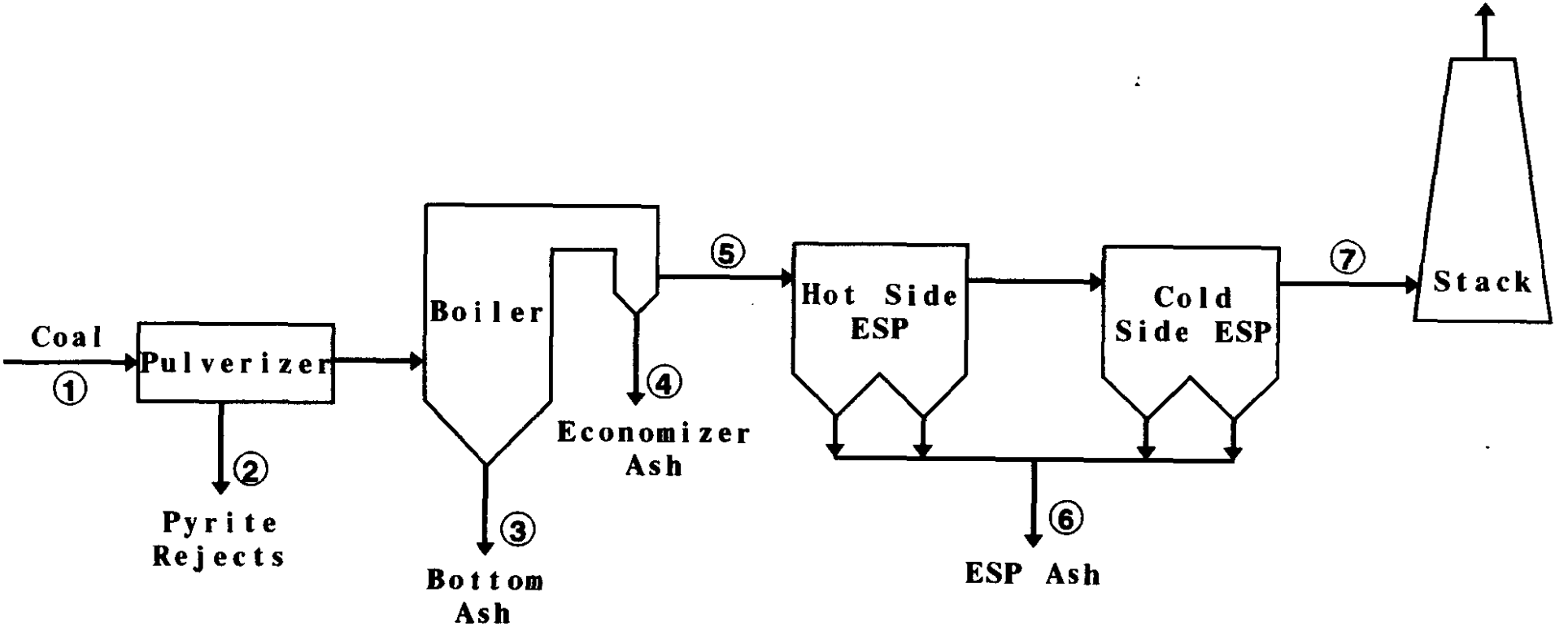

FIGURE 3.12-1. PLANT SMITH FLOW DIAGRAM

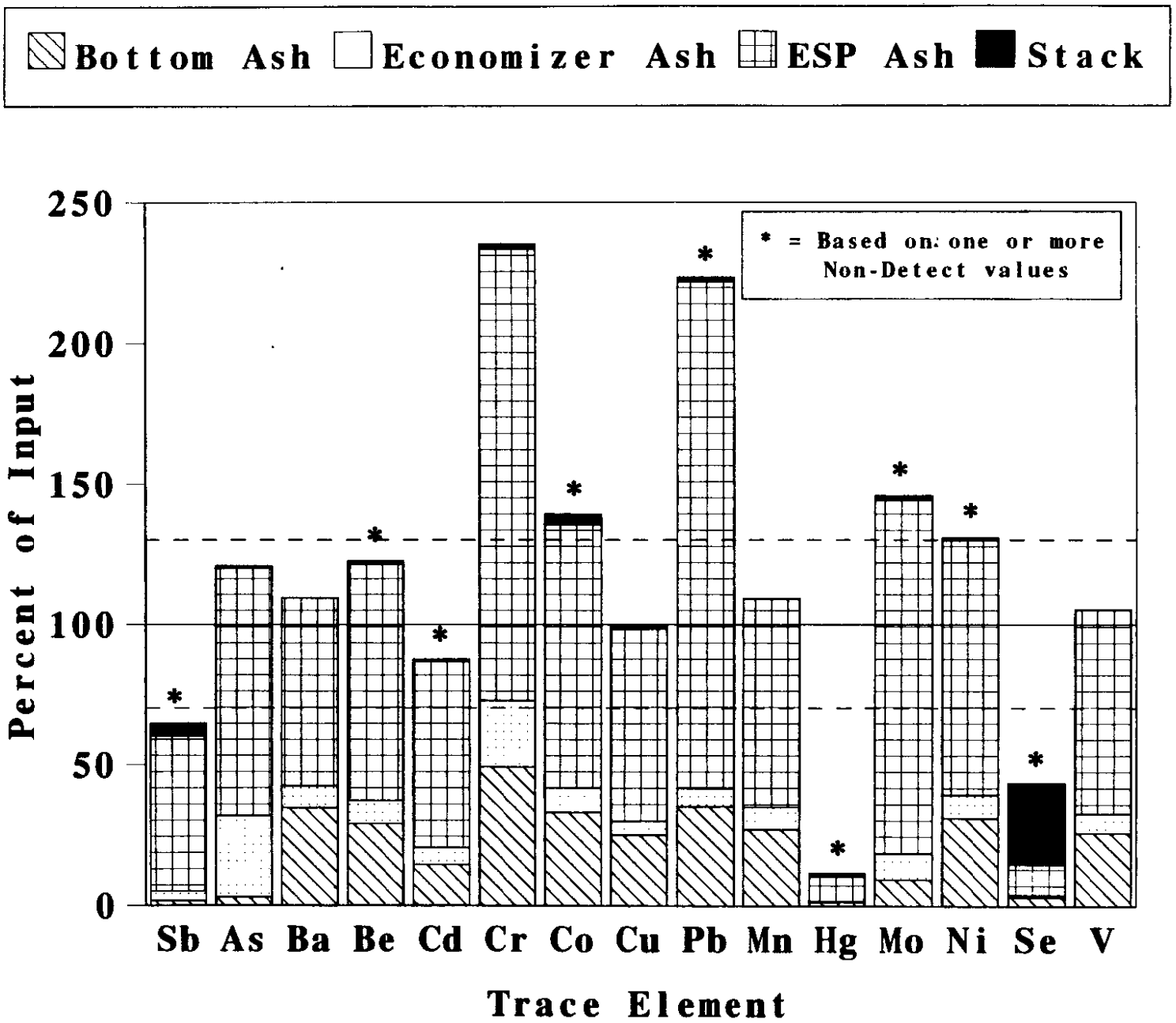

FIGURE 3.12-2. TRACE ELEMENTS IN OUTPUT STREAMS PLANT SMITH, BASELINE TESTS

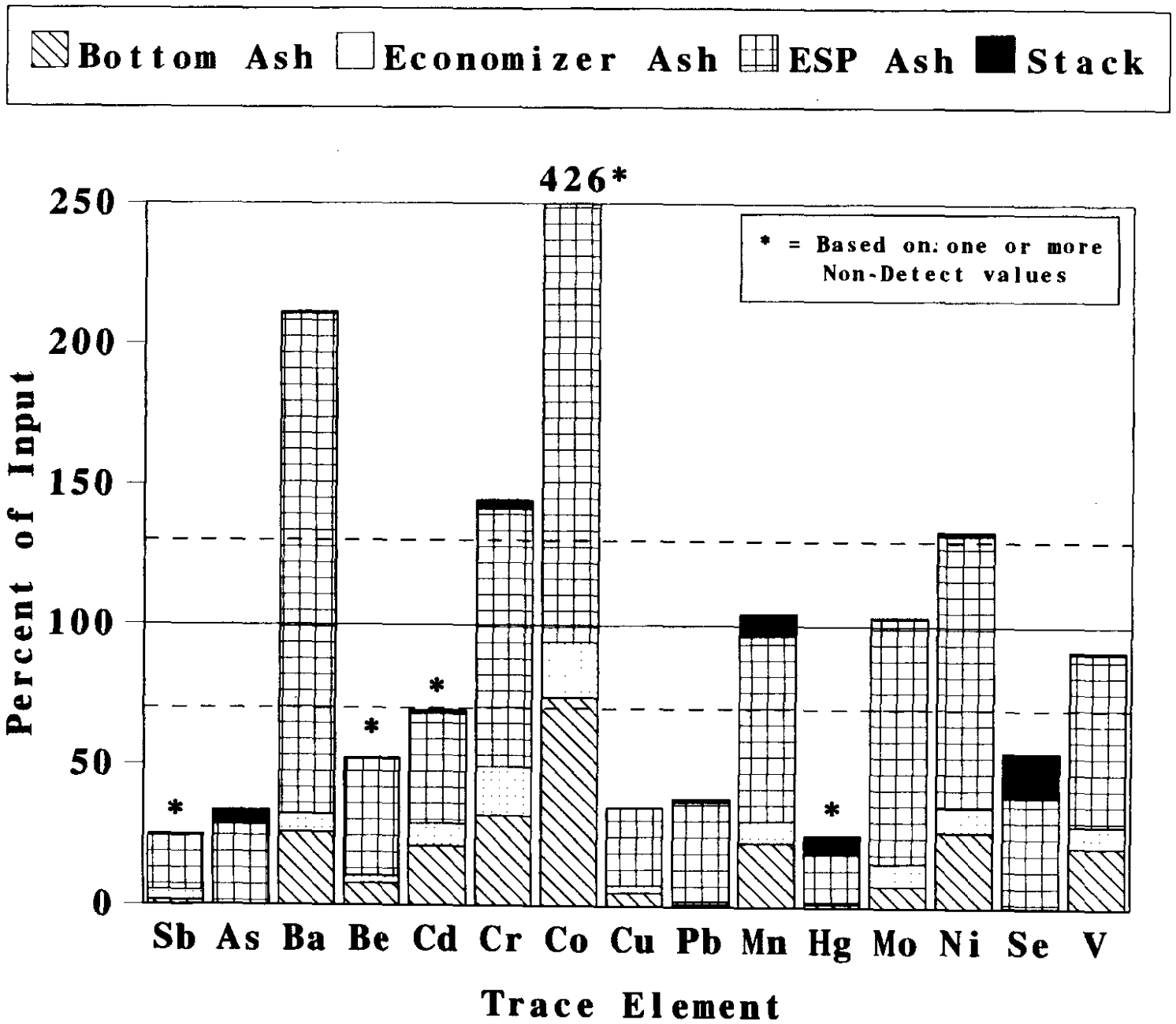

FIGURE 3.12-3. TRACE ELEMENTS IN OUTPUT STREAMS PLANT SMITH, LOW NOx TESTS

Table 3.12-1 Trace Element Flow Rates, Plant Smith, Baseline Tests

	(1) Raw Coal	(2) Pyrite Rejects	(3) Bottom Ash	(4) Economizer Ash	(5) ESP Inlet	(6) ESP Ash	(7) Stack
Units: lb/hr							
Antimony	ND< 0.337 #	0.0072[A]	ND< 0.0061 #	0.0114	0.193	0.185[B]	ND< 0.0152 #
Arsenic	0.319	0.339	0.0092	0.0922	0.296	0.282	0.0022[A]
Barium	4.55	0.338	1.58	0.351	3.19	3.04	0.0074[A]
Beryllium	0.105[A]	ND< 0.034 #	0.0304	0.0087	0.0920	0.0884	ND< 0.0011 #
Cadmium	0.277	0.091[A]	0.0402	0.0164	0.935	0.184	ND< 0.0020 #
Chromium	0.921	0.122[A]	0.453	0.217	1.56	1.48	0.0164
Cobalt	0.268	0.165	0.0885	0.0234	0.261	0.251	ND< 0.0098 #
Copper	0.967	0.0924	0.242	0.0482	0.699	0.661	0.0087
Lead	0.98[C]	1.010	0.344	0.0629	1.83	1.76	ND< 0.0152 #
Manganese	2.82	0.249	0.763	0.224	2.34	2.09	0.0099
Mercury	0.0108	0.0024	ND< 0.00015 #	ND< 0.00004 #	0.0036	ND< 0.0009 #	0.00013
Molybdenum	0.750	0.0391	0.0698	0.0688	0.983	0.944	ND< 0.0114 #
Nickel	1.13	0.789	0.351	0.0935	1.07	1.03	0.011[B]
Selenium	0.096	0.0040[A]	ND< 0.0030 #	0.0008[C]	0.0577	ND< 0.0102 #	0.0276
Vanadium	7.86	0.341	2.03	0.545	5.91	5.67	0.0238[A]

[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes three non-detect measurements
\# Non-detectible in all samples

Table 3.12-2 Trace Element Flow Rates, Plant Smith, Low NO_x Tests

	(1) Raw Coal	(2) Pyrite Rejects	(3) Bottom Ash	(4) Economizer Ash	(5) ESP Inlet	(6) ESP Ash	(7) Stack
Units: lb/hr							
Antimony	ND< 0.653 #	0.014[C]	ND< 0.0108 #	0.0227	0.442	0.125	0.0044[C]
Arsenic	0.383[B]	0.010[C]	N/A	N/A	0.131	0.109	0.019
Barium	5.84	0.284	1.50	0.378	10.7	10.4	0.037
Beryllium	0.214	0.018[A]	0.0167	0.0061	0.093	0.090	ND< 0.0012 #
Cadmium	0.340	0.032	0.0708	0.0272	0.246	0.134	ND< 0.0044[C]
Chromium	1.47	0.207	0.467	0.257	1.53	1.36	0.043
Cobalt	ND< 0.082 #	0.004[C]	0.0605	0.0162	0.279	0.187	0.085
Copper	2.53	0.096	0.121	0.0691	0.709	0.685	0.002[B]
Lead	2.77	0.039	0.021	0.0307	1.03	0.975	0.031
Manganese	2.68	0.124	0.601	0.210	2.06	1.77	0.208
Mercury	0.013	0.00021[B]	ND< 0.00016 #	ND< 0.00010 #	0.0029	0.0021	0.0008
Molybdenum	1.47	0.310	0.113	0.117	1.39	1.28	0.0069
Nickel	1.11	0.127	0.295	0.0958	1.11	1.08	0.015[C]
Selenium	0.336	0.0082	0.00066[A]	0.00027	0.289	0.131	0.053
Vanadium	11.3	1.47	2.41	0.858	7.22	6.94	0.074

[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes three non-detect measurements
Non-detectible in all samples
N/A Not analyzed.

Table 3.12-3 Concentrations and Removal Efficiencies, Plant Smith

	Baseline			Low NOx		
	ESP Inlet, µg/Nm³	ESP Outlet, µg/Nm³	Baseline Removal Efficiency, Percent	ESP Inlet, µg/Nm³	ESP Out, Stack, µg/Nm³	Low NOx Removal Efficiency, Percent
Antimony	128	ND< 24.8 #	> 91.8	298	5.6	> 96.5
Arsenic	195	1.82	99.1	88.4	12.9	85.2
Barium	2,106	5.60	99.6	7,228	24.9	99.6
Beryllium	60.7	ND< 1.35 #	> 98.8	62.4	ND< 1.3 #	> 98.7
Cadmium	618	1.4	> 98.9	166	4.0	> 96.7
Chromium	1,027	17.8	99.1	1,027	41.	97.2
Cobalt	173	8.6	> 96.1	188	4.0	68.8
Copper	461	13.8	98.6	477	6.5	> 99.7
Lead	1,212	21.4	99.1	695	23.	97.0
Manganese	1,544	70.9	99.4	1,383	21.	89.3
Mercury	2.40	0.760	85.7	1.97	0.97	62.5
Molybdenum	649	23.	> 98.8	933	41.	94.9
Nickel	705	12.	> 98.9	745	8.3	98.6
Selenium	38.1	63.7	26.9	195	170.	71.1
Vanadium	3,905	16.	> 99.6	4,858	1.4	98.9

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.

Table 3.12-4 Stream Temperatures, Plant Smith

Temperature, deg F	
Hot-Side ESP Inlet	702
Cold-Side ESP Outlet (To Stack)	330

Section 3.13 R.E. Burger Station

Testing was performed on Boiler #8 of Ohio Edison's R.E. Burger Station located in Dilles Bottom, Ohio, and having a gross generating capacity of 160 MWe. The boiler was designed by Babcock and Wilcox and has been in operation since 1955. Testing was conducted during April and May of 1993. The boiler is wall-fired and burns a medium sulfur (3.5%) bituminous coal from Ohio. The coal burned during the test period averaged about 2% moisture and 12% ash.

Bottom ash is removed from the boiler by an ash sluicing system, and fly ash is removed by a cold-side electrostatic precipitator (ESP) with a design efficiency of 99.35%. Flue gas exiting the ESP is discharged through the stack.

The SNRB™ process was on site as part of a test program being performed by Babcock and Wilcox (B&W) under DOE's Innovative Clean Coal Technology Program. The SNRB™ unit draws a 5-MW (equivalent) slipstream from the boiler. This corresponds to approximately 2% of the total flue gas. The SNRB™ process removes particulates, nitrogen oxides (NO_x), and sulfur oxides (SO_x) from the flue gas. The flue gas exiting the SNRB™ process is then rejoined with flue gas exiting the boiler prior to entering the ESP.

In this process, both dry sorbent (lime) and ammonia are injected upstream of a fabric filter (baghouse). A catalyst for the selective catalytic reduction (SCR) of NO_x is mounted inside the filter bags, providing for the destruction of NO_x as the flue gas/ammonia mixture passes over the catalyst. Sulfur oxides are adsorbed by the sorbent both in the flue gas duct and on the filter bags in the baghouse. Because the NO_x and SO_x removal processes require operation at elevated temperature (550-900°F), special high temperature fabric filter bags are used.

The baghouse consists of six individual modules each containing 42 bag/catalyst assemblies. The baghouse is designed to handle about 48,000 ft^3/min (actual) of flue gas. Flue gas heaters are located at the inlet and outlet of the baghouse to simulate the economizer and the air heater sections, respectively.

Figure 3.13-1 is a process flow diagram of the site while Figure 3.13-2 gives information on trace element partitioning. Tables 3.13-1 and 3.13-2 present trace element flow rates and concentration/removal efficiency data respectively Table 3.13-3 gives stream temperatures at various points in the plant.

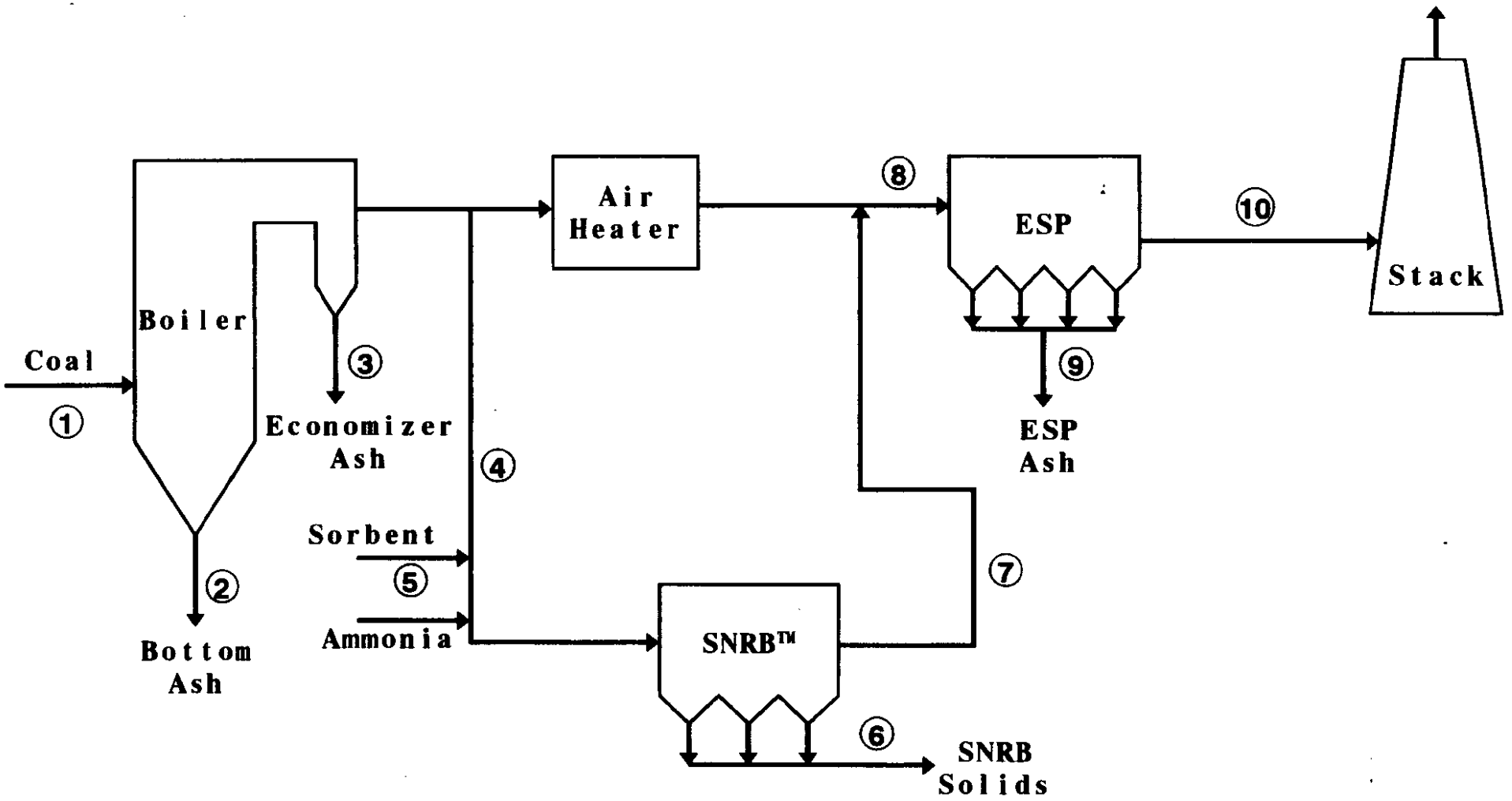

FIGURE 3.13-1. SNRB FLOW DIAGRAM, R.E. BURGER STATION

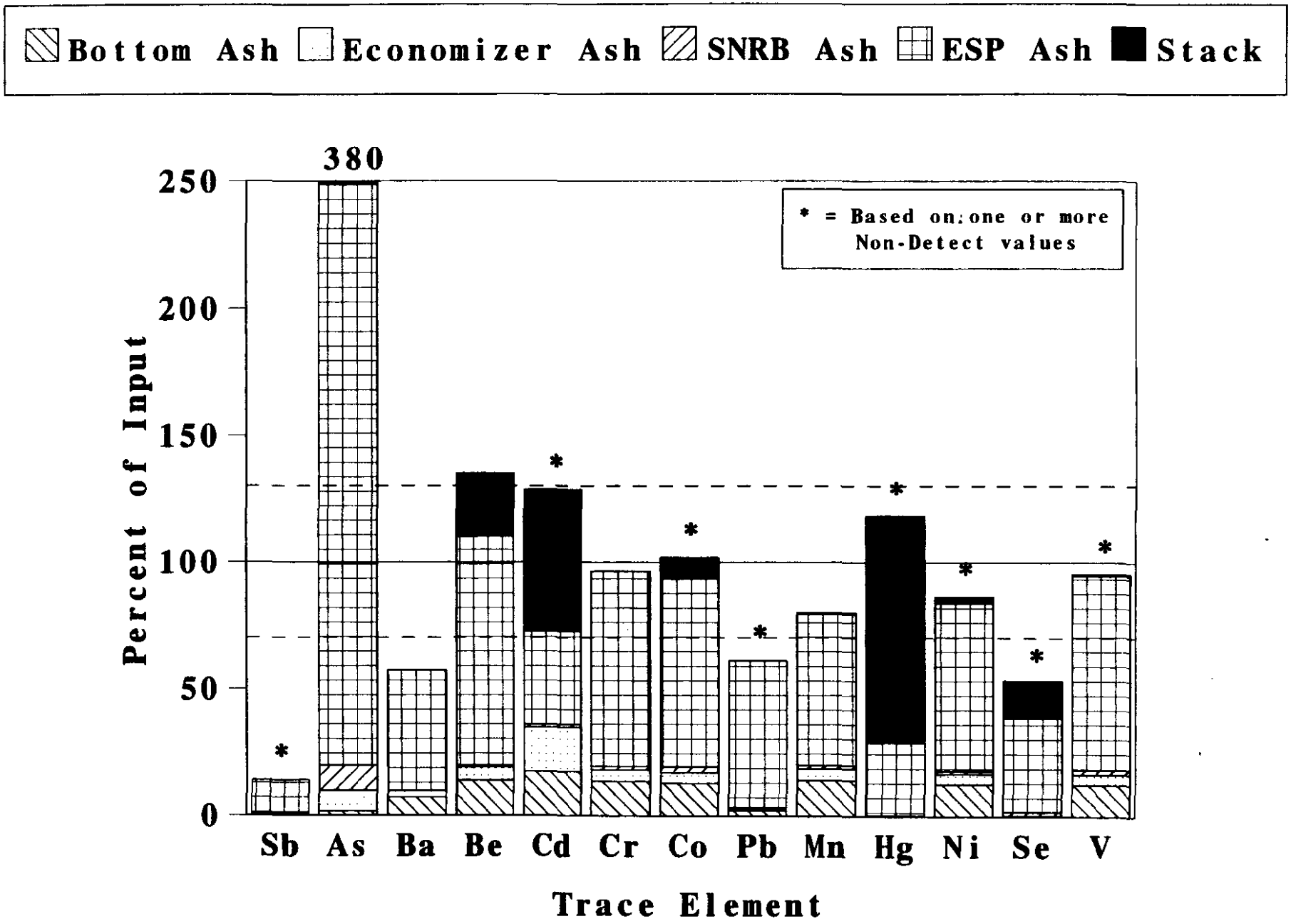

FIGURE 3.13-2. TRACE ELEMENTS IN OUTPUT STREAMS R. E. BURGER STATION, SNRB

Table 3.13-1 Trace Element Flow Rates, R.E. Burger Station, SOx-NOx-ROx-BOx (SNRB)

	(1) Coal Inlet	(2) Bottom Ash	(3) Economizer Ash	(4) SNRB Inlet	(5) Lime Input	(6) SNRB Solids	(7) SNRB Outlet	(8) ESP Inlet	(9) ESP Ash	(10) Stack
Units: lb/hr										
Antimony	ND< 0.124 #	ND< 0.00069[B]	0.00028[B]	0.00023	0.00014	0.00047	0.000028[B]	0.0144[A]	0.0159	0.00017
Arsenic	0.618	0.0108	0.0509	0.0130	0.0007	0.0607	0.000043	0.431	2.22	0.0047
Barium	5.81	0.415	0.145	0.0431	0.0063	0.0068	0.000007[A]	0.850	2.76	0.0018
Beryllium	0.0828	0.0115	0.0043	0.0013	ND< 0.00019 #	0.00065[A]	ND< 0.000513 #	0.0287[A]	0.0749	ND< 0.0209 #
Cadmium	ND< 0.0371 #	0.0065	0.0064	0.00021	ND< 0.00023 #	ND< 0.00040 #	0.000023[A]	0.0043[A]	0.0138	ND< 0.0209 #
Chromium	1.85	0.252	0.0917	0.0222	ND< 0.00037[B]	0.0264	0.00019[B]	0.503[A]	1.42	0.0017
Cobalt	0.284	0.0367	0.0120	0.0045	0.0013	0.0068	ND< 0.00062[B]	0.0862[B]	0.211	ND< 0.0248 #
Lead	0.655	0.0141	0.0040	0.0053	ND< 0.00014 #	0.0032	0.000019[A]	0.168[A]	0.378	ND< 0.00035[B]
Manganese	2.35	0.330	0.110	0.0221	0.0023	0.0291	0.000029[A]	0.503	1.40	0.0170[A]
Mercury	0.0161	ND< 0.00005 #	ND< 0.00002[B]	0.00028	ND< 0.000009 #	ND< 0.00002 #	0.00050[A]	0.0156[A]	0.0046	0.0144
Nickel	0.989	0.124	0.0403	0.0107	ND< 0.00009 #	0.0116	0.0018[A]	0.227[A]	0.654	ND< 0.0248 #
Selenium	0.334	ND< 0.0011 #	ND< 0.00038 #	0.0042	ND< 0.0002 #	0.0047	ND< 0.00001 #	0.156[A]	0.123	0.0497
Vanadium	2.72	0.339	0.112	0.0317	0.0016	0.0487	ND< 0.0005 #	0.802[A]	2.08	ND< 0.0222[A]

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.13-2 Concentrations and Removal Efficiencies, R.E. Burger Station

	SNRB			ESP		
	SNRB Inlet, µg/Nm³	SNRB Outlet, µg/Nm³	Removal Efficiencies, Percent	ESP Inlet, µg/Nm³	Stack, µg/Nm³	Removal Efficiencies, Percent
Antimony	8.7	0.815	88.2	12	0.13	98.8
Arsenic	493	1.26	99.7	360	3.6	98.9
Barium	1630	0.195	99.98	710	1.4	99.8
Beryllium	48.3	ND< 16. #	> 58.1	24	ND< 16. #	> 25.4
Boron						
Cadmium	7.76	0.685	88.9	3.6	ND< 16. #	Neg
Chromium	839	5.64	99.2	420	1.3	99.7
Cobalt	170	ND< 19. #	> 85.7	72	ND< 19. #	> 70.9
Copper						
Lead	199	0.563	99.6	140	ND< 0.27 #	> 99.8
Manganese	837	0.86	99.9	420	13	96.7
Mercury	10.6	14.5	Neg	13	11	3.1
Nickel	404	52.5	83.7	190	ND< 19. #	> 89.2
Selenium	157	ND< 0.34 #	> 99.7	130	38	67.8
Vanadium	1200	ND< 17. #	> 98.2	670	ND< 17. #	> 97.2

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.

Table 3.13-3 Stream Temperatures, R.E. Burger Station

Temperature, deg F	
SNRB Inlet	639
Baghouse Inlet	865
SNRB Outlet	793
ESP Inlet	317
ESP Outlet	321

Section 3.14 Arapahoe Station

Plant Description

The Public Service of Colorado's Arapahoe Station was used for this test. The boiler for the test unit is a 115 MWe, roof-fired boiler that was fired on a western bituminous coal during the test period. This particular boiler is also capable of burning natural gas.

Low NO_x burners and overfire air ports have been installed for NO_x control. The test unit is also equipped with a selective non-catalytic reduction (SNCR) unit that utilizes a urea injection system. The SNCR unit was operated during one phase of the test program. Particulate removal is accomplished with a fabric filter dust collector (FFDC) having an air-to-cloth ratio of 2. The design of the FFDC calls for particulate removal down to 0.007 grains/dry standard cubic foot. No SO_2 removal system was used during the test period, although this unit will use sorbent injection upstream of the FFDC in the future.

Bottom ash consists of the larger ash particles, including those removed from the boiler surfaces during soot blowing. The bottom ash is discharged to a hopper from which it is sluiced into the ash pit water box and grinder. From there it is transported to the settling pond. Solids are periodically removed from the settling pond and transported off-site for disposal. Fly ash is discharged into a series of hoppers and is then pneumatically conveyed to a flyash silo. It is then transported off-site for disposal.

A schematic flow diagram is presented in Figure 3.14-1. Figures 3.14-2 and 3.14-3 present partitioning results for the trace elements during these same periods. Tables 3.14-1 and 3.14-2 present trace element flow rates results during baseline operation and SNCR testing, respectively. Table 3.14-3 gives trace element

concentrations and removal efficiencies during both periods. Temperature data was not available at this plant.

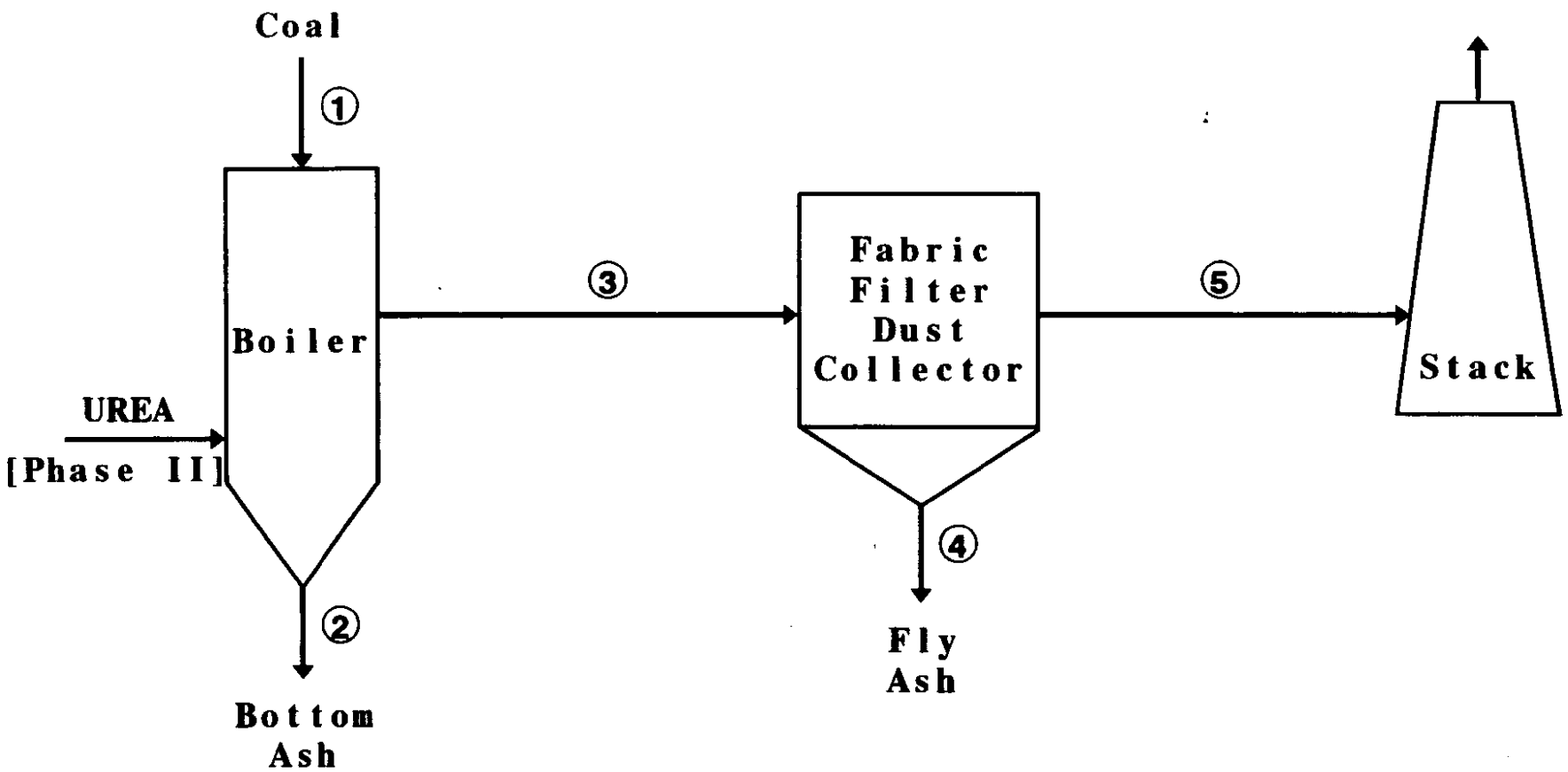

FIGURE 3.14-1. PUBLIC SERVICE OF COLORADO ARAPAHOE STATION FLOW DIAGRAM

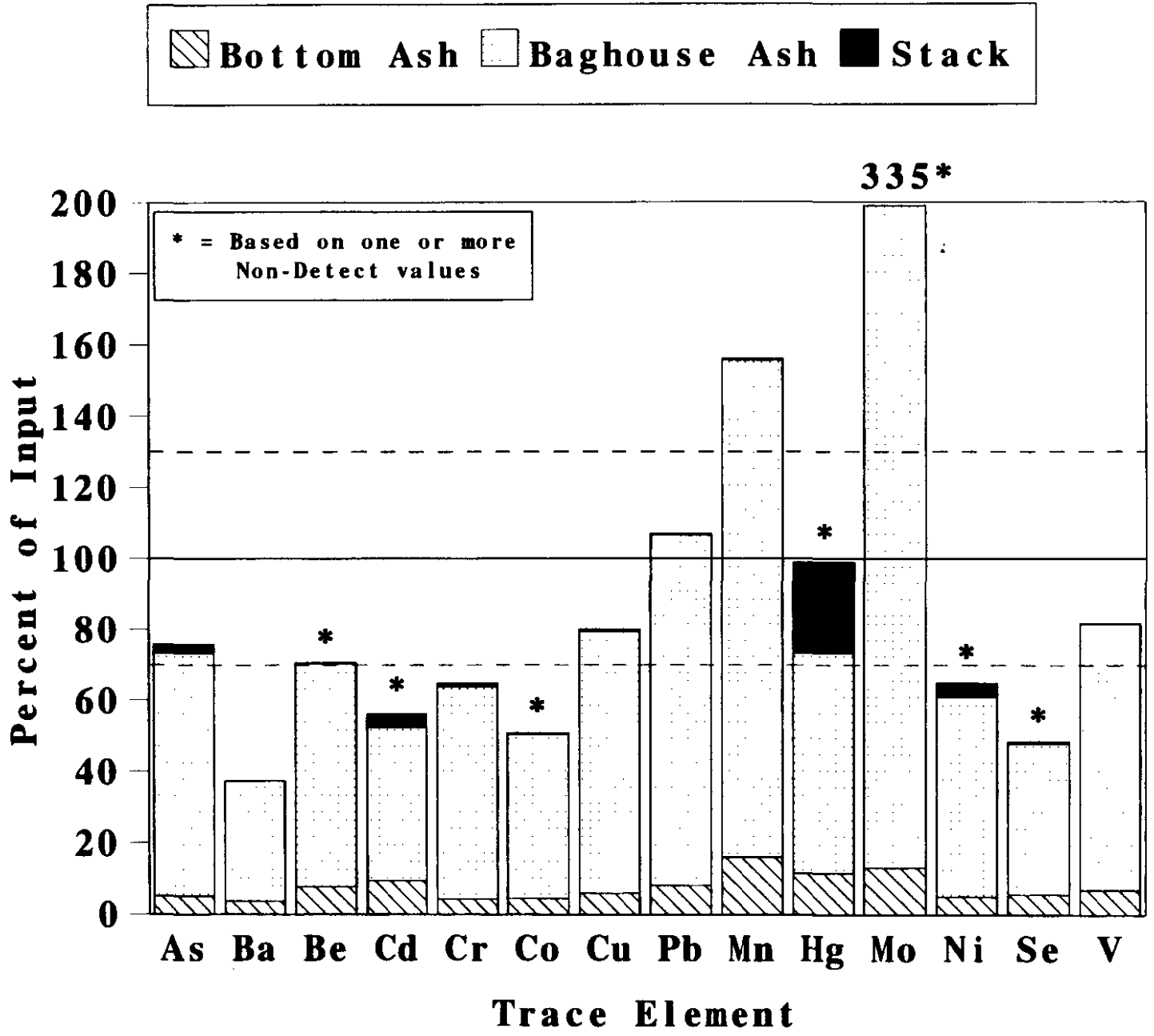

FIGURE 3.14-2. TRACE ELEMENTS IN OUTPUT STREAMS ARAPAHOE STATION, BASELINE TESTS

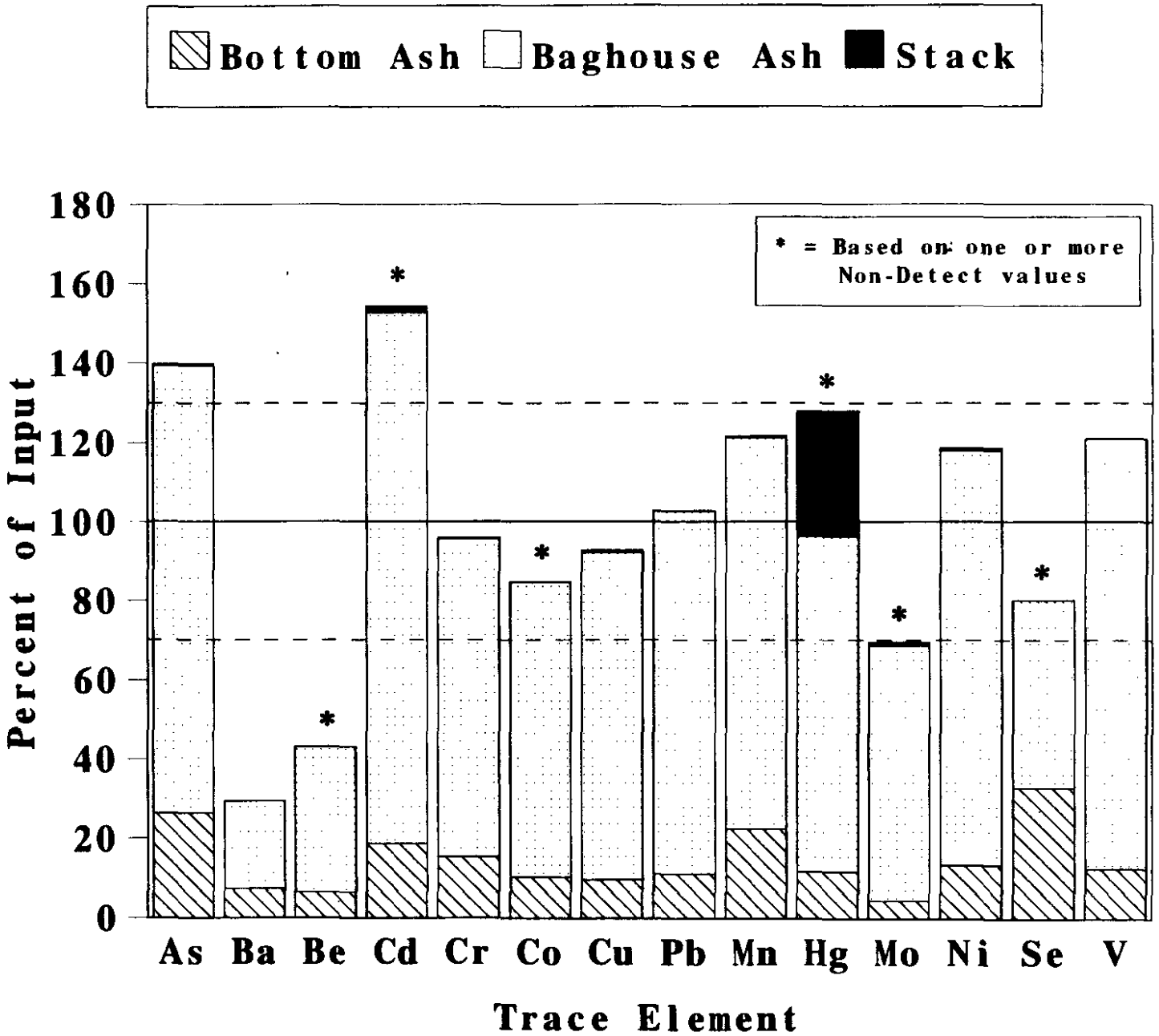

FIGURE 3.14-3. TRACE ELEMENTS IN OUTPUT STREAMS ARAPAHOE STATION, SNCR

Table 3.14-1 Trace Element Flow Rates, Arapahoe Station, (Baseline)

	(1) Coal In	(2) Bottom Ash	(3) Baghouse Inlet	(4) Baghouse Ash	(5) Stack
Units: lb/hr					
Arsenic	0.0376	0.0019	0.0281	0.0256	0.00091
Barium	32.8	1.22	0.285	11.0	0.00136
Beryllium	0.0172	0.0013	0.0109	0.0108	ND< 0.000028 #
Cadmium	ND< 0.0039[B]	ND< 0.00037 #	0.0028	ND< 0.0017[B]	0.00014
Chromium	0.0861	0.0037	0.0608	0.0513	0.00080
Cobalt	0.0705	0.0031	0.0363	0.0324	ND< 0.00026 #
Copper	0.211	0.0127	0.206	0.155	0.00133
Lead	0.164	0.0134	0.0775	0.162	0.00053
Manganese	0.329	0.0531	0.236	0.459	0.00121
Mercury	0.0016	0.00019[B]	0.0016	0.0010[A]	ND< 0.00042 #
Molybdenum	0.0078[B]	ND< 0.0010[A]	0.0131	0.0250	0.00021
Nickel	0.0470	ND< 0.0024[B]	0.0368	0.0263	0.00179
Selenium	0.0642	ND< 0.0037 #	0.0272	0.0270	0.00044
Vanadium	0.235	0.0162	0.165	0.175	0.00029

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.14-2 Trace Element Flow Rates Arapahoe Station, (SNCR)

	(1) Coal In	(2) Bottom Ash	(3) Baghouse Inlet	(4) Baghouse Ash	(5) Stack
Units: lb/hr					
Arsenic	0.0538	0.0142	0.0154	0.0608	0.00018
Barium	28.5	2.12	0.229	6.23	0.00126
Beryllium	0.0462	0.0030	0.0089	0.0169	ND< 0.000029 #
Cadmium	ND< 0.0050 #	ND< 0.00094 #	0.0024	ND< 0.0068 #	ND< 0.000087 #
Chromium	0.118	0.0181	0.0605	0.0946	0.00036
Cobalt	0.109	0.0113	0.0313	0.0811	ND< 0.00028 #
Copper	0.311	0.0302	0.245	0.257	0.00164
Lead	0.185	0.0208	0.0541	0.169	0.00048
Manganese	0.437	0.0981	0.105	0.432	0.00106
Mercury	0.0016	ND< 0.00019 #	0.0023	0.0014	0.00050[A]
Molybdenum	0.0420	ND< 0.0019 #	0.0141	0.0270	0.00033
Nickel	0.0840	0.0113	0.0350	0.0878	0.00058
Selenium	0.126	ND< 0.0415 #	0.0142	ND< 0.0594[B]	ND< 0.000077 #
Vanadium	0.361	0.0453	0.143	0.392	0.00034

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.14-3 Concentrations and Removal Efficiencies, Arapahoe Station

	Baseline			SNCR		
	Baghouse Inlet, µg/Nm³	Baghouse Outlet, µg/Nm³	Removal Efficiencies, Percent	Baghouse Inlet, µg/Nm³	Baghouse Outlet, µg/Nm³	Removal Efficiencies, Percent
Arsenic	30	0.97	96.8	16.2	0.19	98.8
Barium	304.7	1.45	99.5	241	1.31	99.5
Beryllium	11.7	ND< 0.03 #	> 99.7	9.4	ND< 0.03 #	> 99.8
Cadmium	2.96	0.15	94.9	2.5	ND< 0.09 #	> 98.2
Chromium	65	0.85	98.7	63.7	0.37	99.4
Cobalt	38.8	ND< 0.28 #	> 99.3	33	ND< 0.29 #	> 99.6
Copper	220	1.42	99.4	258	1.7	99.3
Lead	82.9	0.56	99.3	57	0.5	99.1
Manganese	252.8	1.29	99.5	111	1.1	99.0
Mercury	1.72	ND< 0.45 #	> 73.7	2.4	0.52	77.9
Molybdenum	14	0.22	98.4	14.8	0.34	97.7
Nickel	39.3	1.9	95.1	36.8	0.6	98.5
Selenium	29.1	0.47	98.4	15	ND< 0.08 #	> 99.7
Vanadium	176	0.31	99.8	151	0.35	99.8

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.

Section 3.15 TIDD PFBC Demonstration

Plant Description

The TIDD PFBC demonstration, located in Brilliant, Ohio, is operated by Ohio Power Company, a subsidiary of American Electric Power (AEP). The boiler at the TIDD site is a bubbling-bed, pressurized fluidized bed combustor (PFBC) rated at 70 MWe full load. Total plant load during the test period was 45 to 46 MW; 37 MW was produced by a steam turbine generator and 8 MW was produced by depressurizing the hot flue gases through a gas turbine generator. The process operating conditions for the unit were selected by AEP and represent typical long-term operating conditions for the process.

Crushed coal (Pittsburgh No. 8, bituminous) is combined with water from a nearby river to produce a coal paste which was approximately 25 weight percent moisture. The paste is fed to the combustion chambers along with crushed dolomite. The material is fluidized by high velocity combustion air in the water-cooled boiler. Mean bed temperatures in the combustion chambers were controlled at approximately 1500°F during the test period. As the coal is combusted, the calcium carbonate in the dolomite or limestone is calcined to form quicklime which then reacts with the SO_2 and oxygen in the combustion gases to form solid calcium sulfate. This reaction removes SO_2 from the combustion gases, thus controlling SO_2 emissions. Test data from this program show approximately 90% removal of sulfur dioxide in the combustor. Formation of nitrogen oxides (NO_x) is minimized because of the relatively low combustion temperature of the PFBC process.

After releasing heat to the in-bed, water-cooled boiler tubes, the particulate-laden combustion gases flow into seven parallel, two-step cyclones. These cyclones remove approximately 93% of the entrained solids (primarily sulfated lime, unreacted lime, ash, and

unburned carbon) from the gases. The combustion gases then flow to the gas turbine where they are expanded and then exit through the turbine exhaust gas economizer. Final particulate removal from the gases is achieved in an electrostatic precipitator (ESP) before the gases are released to the atmosphere.

Bed ash, which comprises about 45% of the total ash produced, is periodically removed from the bottom of the combustor through a lock hopper system. Solids collected by the primary cyclone are transported to a storage silo. Secondary cyclone solids are combined with the material collected in the ESP. All solids are transported by truck off site for disposal.

A research feature of the TIDD facility is a demonstration-scale hot gas cleanup (HGCU) system. Treated gas from one of the seven cyclone systems (approximately one-seventh of the total gas flow from the combustor) is diverted to a ceramic barrier, advanced particle filter (APF) and back-up cyclone, and directed back to the outlet header of the secondary cyclones. The APF uses silicon carbide candles in a cluster/plenum arrangement developed by Westinghouse Corporation to filter the gas. Tempering air was added to the system during the test period to control ash bridging within the APF system, reducing the APF inlet gas temperature from 1500°F to approximately 1350°F. Entrained solids removed in the APF system are collected and transported by truck off site for disposal.

Figure 3.15-1 shows a simple schematic of the unit. Figure 3.15-2 shows trace element partitioning results. Table 3.15-1 and 3.15-2 present the trace element flow rates and concentration/removal efficiency results. Table 3.15-3 gives stream temperatures at various points in the plant.

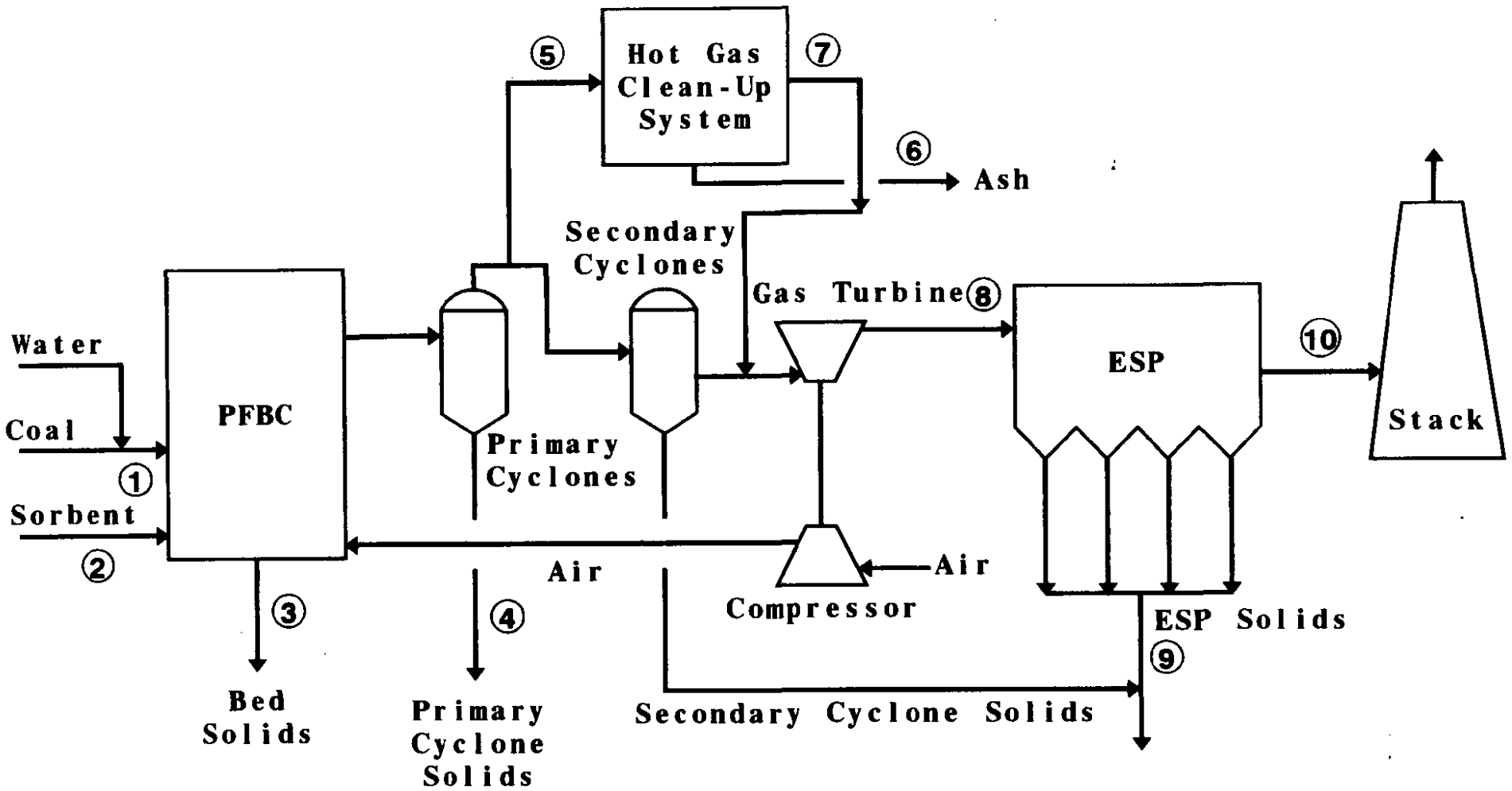

FIGURE 3.15-1. TIDD PFBC DEMONSTRATION FLOW DIAGRAM

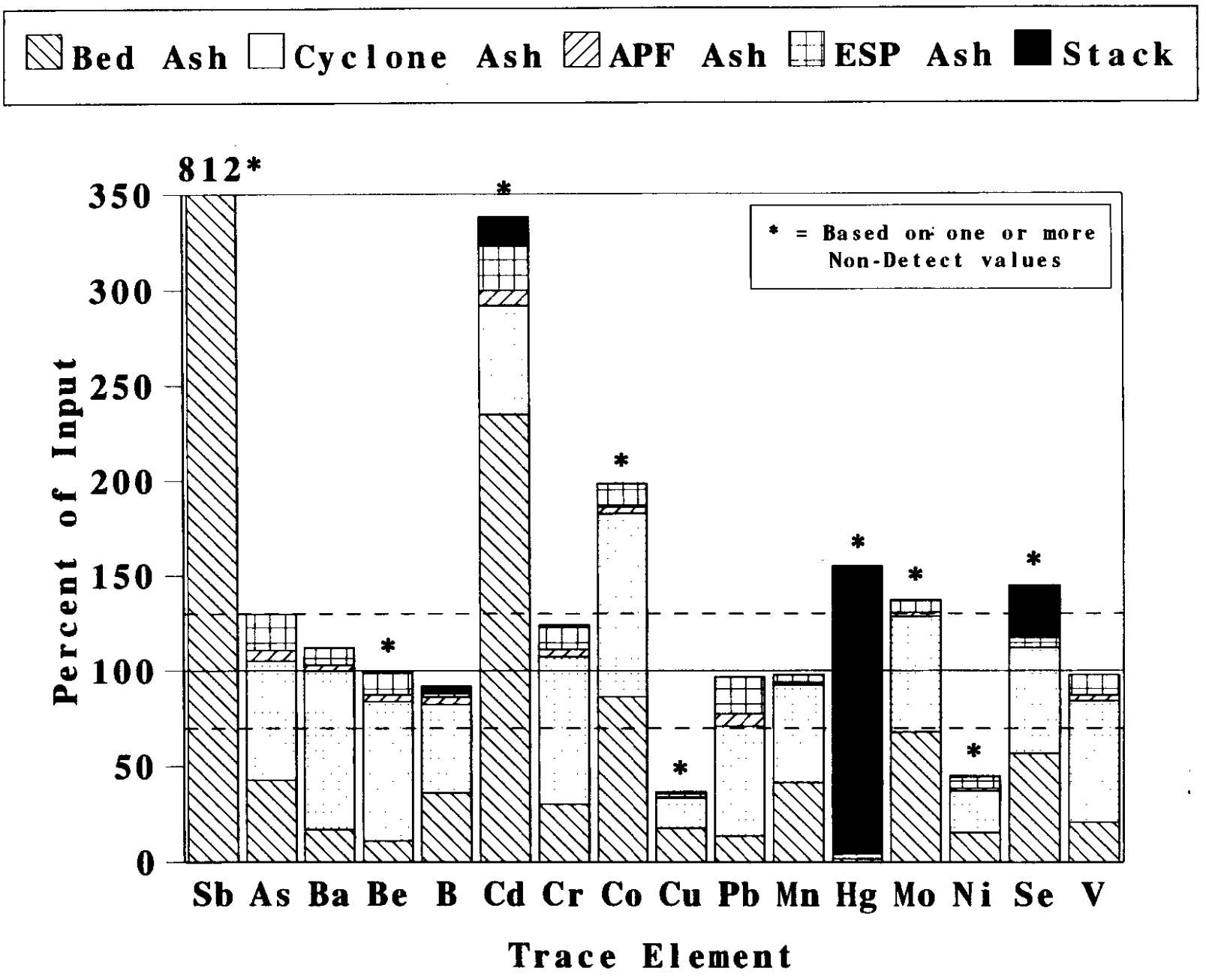

FIGURE 3.15-2. TRACE ELEMENTS IN OUTPUT STREAMS PLANT TIDD, PFBC

Table 3.15-1 Trace Element Flow Rates, TIDD PFBC Demonstration

	(1) Coal Paste	(2) Limestone	(3) Bed Ash	(4) Cyclone Ash	(5) APF In	(6) APF Ash	(7) APF OuT	(8) ESP In	(9) ESP Ash	(10) Stack
Units: lb/hr										
Antimony	0.016	ND< 0.105 #	ND< 0.502	ND< 0.414	ND< 0.00007 #	ND< 0.0157 #	ND< 0.00003 #	ND< 0.044 #	ND< 0.046	ND< 0.0011 #
Arsenic	1.51	0.036	0.661	0.962	0.083	0.085	0.00029	0.245	0.295	0.00053
Barium	1.81	0.067	0.316	1.55	0.065	0.063	0.000003	0.140	0.171	0.00039
Beryllium	0.054	ND< 0.00059[B]	0.0060	0.039	0.0020	0.0020	0.000002	0.0050	0.0062	0.00001[B]
Boron	1.84[A]	0.627	0.893	1.14	0.017	0.097	0.027	0.117	0.047	0.089
Cadmium	0.0037	0.0027	ND< 0.015	0.0036	ND< 0.0005 #	0.0005	ND< 4e-7 #	0.0019	0.0015	0.00095
Chromium	0.535	0.0532	0.177	0.455	0.039	0.023	0.0045	0.076	0.073	ND< 0.0019 #
Cobalt	0.130	ND< 0.0095[B]	0.121	0.134	0.0053	0.0050	0.00002	0.013	0.017	0.00010
Copper	0.234	ND< 0.0089 #	ND< 0.043	ND< 0.038	0.011	ND< 0.0013	0.00006	0.0064[A]	0.0050	0.0022
Lead	0.211	0.131	0.047	0.196	0.018	0.022	0.000002	0.043	0.065	0.00034[B]
Manganese	0.870	1.37	0.931	1.14	0.035	0.031	0.00061	0.082	0.085	0.0036[A]
Mercury	0.0050	ND< 0.00023 #	ND< 0.00009	ND< 0.00012	0.0012	ND< 0.000004	0.0011	0.0093	ND< 0.000009	0.0079
Molybdenum	0.019	0.029	ND< 0.033	ND< 0.029	0.0019	ND< 0.0010	0.00068	ND< 0.0020 #	ND< 0.0029	0.00013[A]
Nickel	0.435	0.228	ND< 0.102	0.145	0.0165	0.0091	0.0038	0.033	0.039	0.0032
Selenium	0.060	0.015	0.043	0.041	0.0050	ND< 0.00031	0.0037	0.036	0.0038	0.021
Vanadium	0.803	0.093	0.186	0.569	0.029	0.027	0.00015	0.070	0.093	0.00053

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.15-2 Concentrations and Control Device Removal Efficiencies, TIDD PFBC Demonstration

	APF In, µg/Nm³	APF Out, µg/Nm³	ESP In, µg/Nm³	Stack, µg/Nm³	APF Removal Efficiency, Percent	ESP Removal Efficiency, Percent
Antimony	0.96	ND< 0.36	ND< 76. #	ND< 2.1 #	> 65	NC
Arsenic	1,100	3.9	420	1.0	99.6	99.8
Barium	860	0.038	240	0.74	99.996	99.7
Beryllium	27	0.02	8.6	0.021	> 99.9	99.8
Boron	220	360	200	170	NC	NC
Cadmium	6.8	ND< 0.005	3.2	1.8	> 99.9	44
Chromium	520	60	130	3.7	89^A	97.2
Cobalt	70	0.3	23	ND< 0.19 #	99.6	> 99.2
Copper	150	0.8	11	4.1	99.5	62
Lead	240	0.029	73	0.65	99.99	99.1
Manganese	460	8.1	140	6.9	98.2^A	95.2
Mercury	16	15	16	15	9	4
Molybdenum	25	9.1	ND< 3.4 #	0.25	63^A	NC
Nickel	220	51	57	6	77^A	90
Selenium	67	49	62	39	27	37
Vanadium	390	2	120	1.0	99.5	99.2

^A May not be representative of actual APF performance.
NC Not calculated. Substance was not detected in the inlet gas stream.
> Indicates the reported removal efficiency is a lower limit. Detection limit was used to estimate a lower limit for the removal efficiency.
ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.

Table 3.15-3 Stream Temperatures, TIDD PFBC Demonstration

Temperature, deg F	
Pressurized Fluid Bed	1500
Hot Gas Cleanup Unit	1350
Gas Turbine	---
ESP Inlet	---
Stack	404

Section 3.16 AirPol GSA System

Plant Description

A flexible pilot plant was constructed at TVA's National Center for Emissions Research to demonstrate the AirPol Gas Suspension Absorption (GSA) process. Flue gas for the pilot plant is drawn from a pulverized coal-fired boiler at the TVA's Shawnee Power Plant. A 9.43 Nm^3/sec (21,463 scfm) slipstream of flue gas from the boiler (approximately 10 MWe equivalent) is taken downstream of a mechanical particulate collector. The slipstream passes through a cross-flow preheater to allow control over the flue gas temperature at the demonstration plant inlet. Fly ash removed in the mechanical collector is reinjected into the demonstration plant to simulate various inlet particulate loadings.

The main components of the GSA pilot plant are the following:

- Slurry preparation system;
- Reactor;
- Cyclone separator;
- Electrostatic precipitator;
- Pulse-jet baghouse.

The lime slurry is prepared from hydrated lime in a batch mixer and pumped to a storage tank. The slurry is pumped from the storage tank to the GSA reactor, where it is injected upward through a two-fluid atomizer near the bottom of the reactor. The quantity of lime used is based on the SO_2 content of the flue gas and the amount of SO_2 removal required. Trim water is added to cool the gas to the design temperature of approximately 62 to 68°C (145-155°F).

The SO_2-laden flue gas from the preheater enters the bottom of the GSA reactor and flows upward. Most of the water in lime slurry

droplets, heated by the flue gas, evaporates in the reactor, decreasing the gas temperature and leaving semi-dry solids. At a gas temperature close to the adiabatic saturation temperature, SO_2 (and to a lesser extent HCl and SO_3) is absorbed by the lime. The resulting solids and unreacted lime are entrained in the flue gas along with the fly ash from the boiler. The flue gas passes up through the reactor and exits at the top into a cyclone-type mechanical collector. The cyclone removes most of the particles from the flue gas (90+ percent), and nearly all of these solids are recycled to the reactor via a screw conveyor, thereby increasing lime utilization. The remaining solids are discharged in the form of a dry by-product. The absorption reactions are thought to take place primarily in the thin layer of fresh lime slurry coating the dry recycle solids; thus the surface area added by the recycled fly ash enhances both the SO_2 removal and the drying process in the reactor. The system is relatively forgiving to atomizer problems (e.g., pluggage, erosion) since SO_2 removal continues to occur via the recycled solids for short periods of time even when the atomizer is removed for maintenance. The high concentration of solids (approximately 200-800 grains/scf) is thought to simultaneously clean the inner surface of the reactor.

The flue gas from the cyclone flows to an electrostatic precipitator for final particulate removal. The solids collected in the ESP are conveyed mechanically to a waste silo. In addition, a slipstream (approximately 1 MWe equivalent or approximately 10%) of the flue gas from the main GSA/ESP plant may be removed from the ESP inlet or outlet, passed through a pulsed-jet baghouse, and returned to the main plant ductwork downstream of the ESP. The baghouse has a nominal air-to-cloth ratio of 4.0 $acfm/ft^2$ and the bags are cleaned by a low-pressure, high-volume, ambient air stream delivered by a rotating manifold. The solids collected in the baghouse are conveyed pneumatically to the waste silo. The treated flue gas is passed to an induced draft fan, reheated, and discharged to the atmosphere through a stack.

Tests were run during four periods:

- Baseline tests (no sorbent) - ESP/baghouse in series
- Demonstration tests - ESP/baghouse in series
- Baseline tests - ESP/baghouse in parallel
- Demonstration tests - ESP/baghouse in parallel

Two slightly different modes of operation were employed during demonstration tests. During the series configuration demonstration tests, the input calcium-to-sulfur ratio (Ca/S) was held constant at 1.4 and the SO_2 removal was allowed to vary. During the parallel configuration demonstration tests, Ca/S was varied to maintain overall SO_2 removal constant at approximately 90 percent. The target approach to saturation temperature was 6.7°C (12°F) for both demonstration test configurations.

Figure 3.16-1 shows the flow diagram for the GSA System and Figures 3.16-2 through 3.16-5 show partitioning results for the four periods described previously. Tables 3.16-1 through 3.16-4 show trace elements flow rates for the four periods. Tables 3.16-5 and 3.16-6 present concentration and removal efficiency data for trace elements during these periods. Table 3.16-7 gives stream temperatures at various points in the plant.

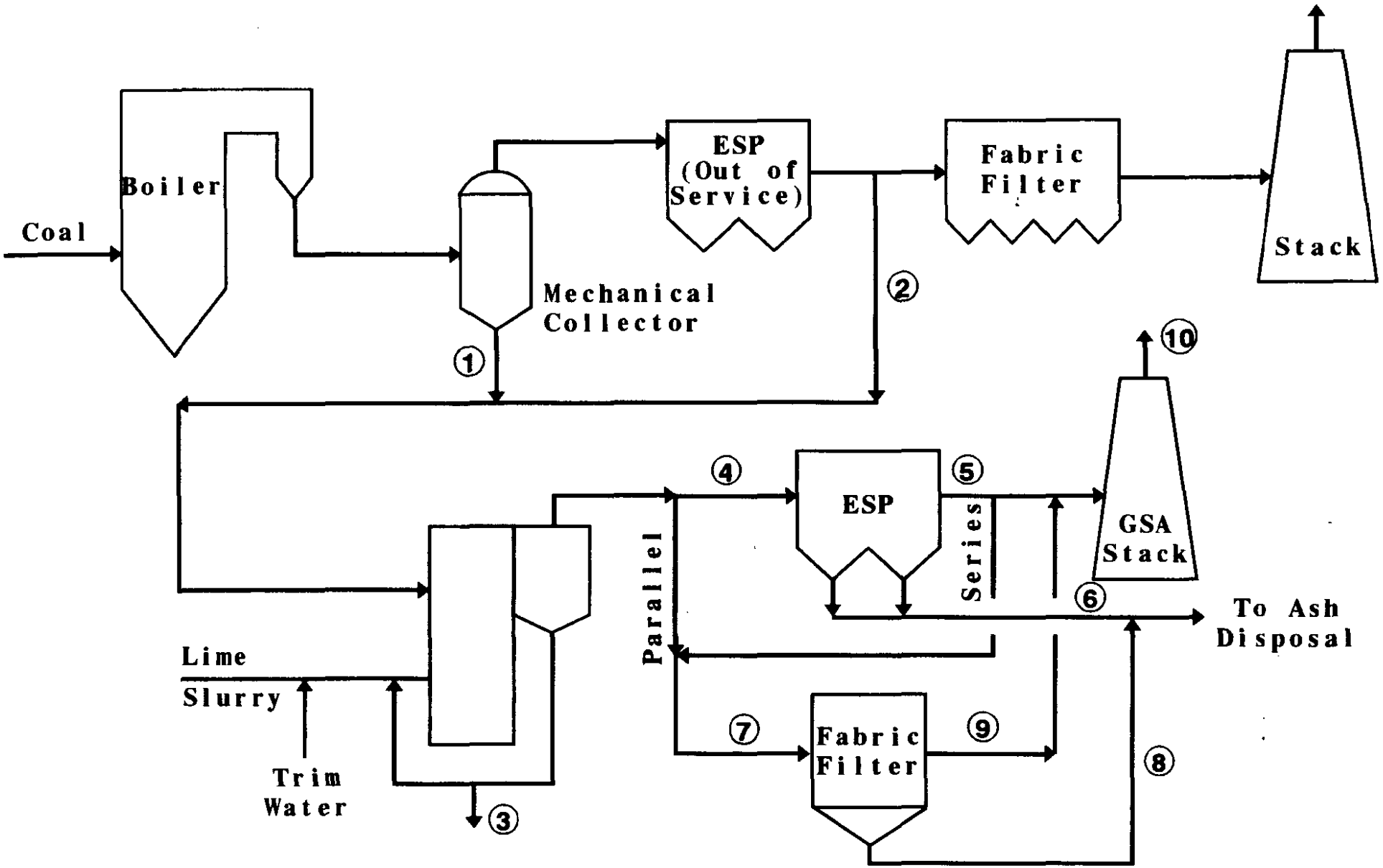

FIGURE 3.16-1. GAS SUSPENSION ABSORPTION SYSTEM AT SHAWNEE POWER PLANT

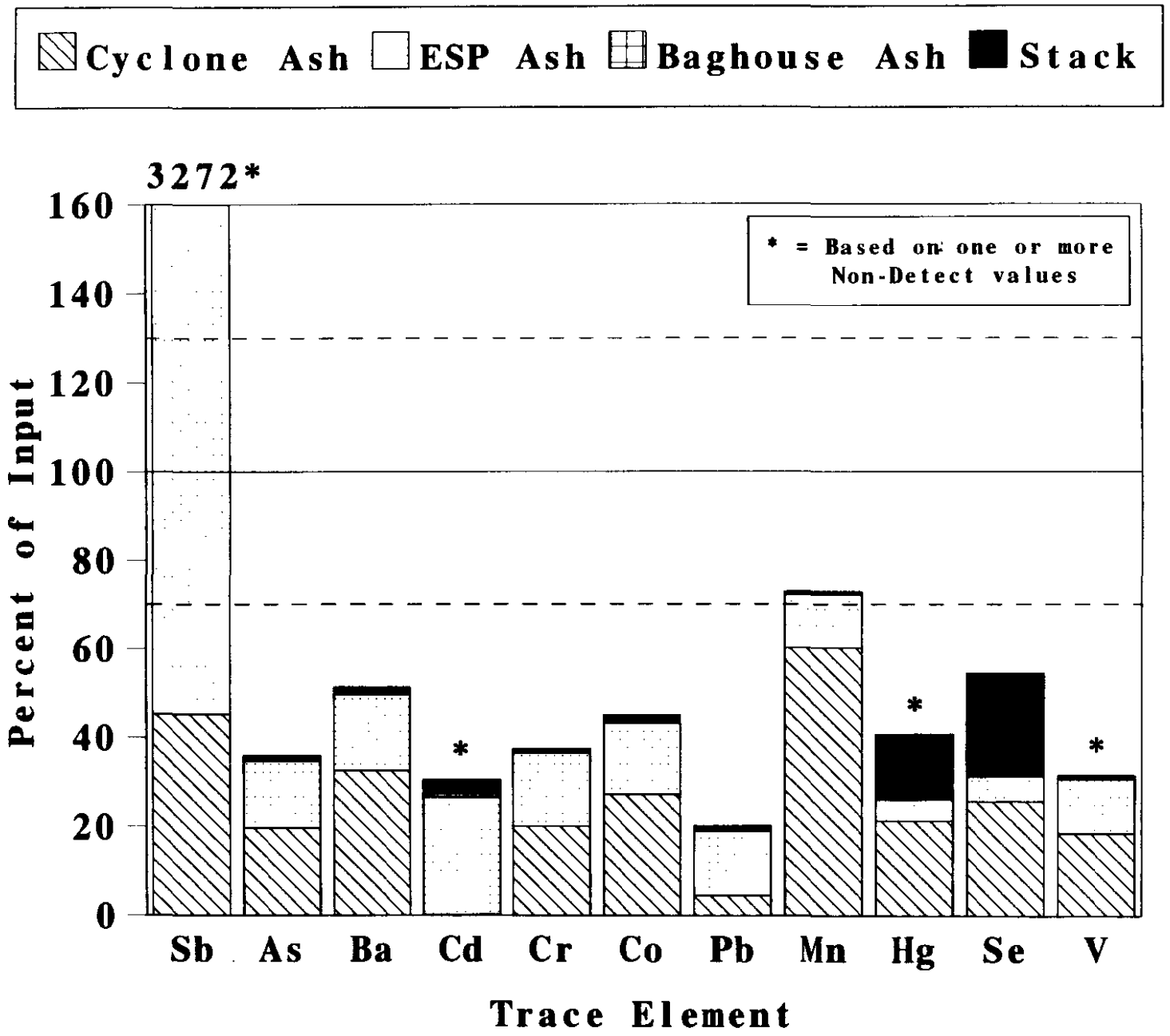

FIGURE 3.16-2. TRACE ELEMENTS IN OUTPUT STREAMS AIRPOL GSA SYSTEM, SERIES CONFIGURATION, BASELINE TESTS

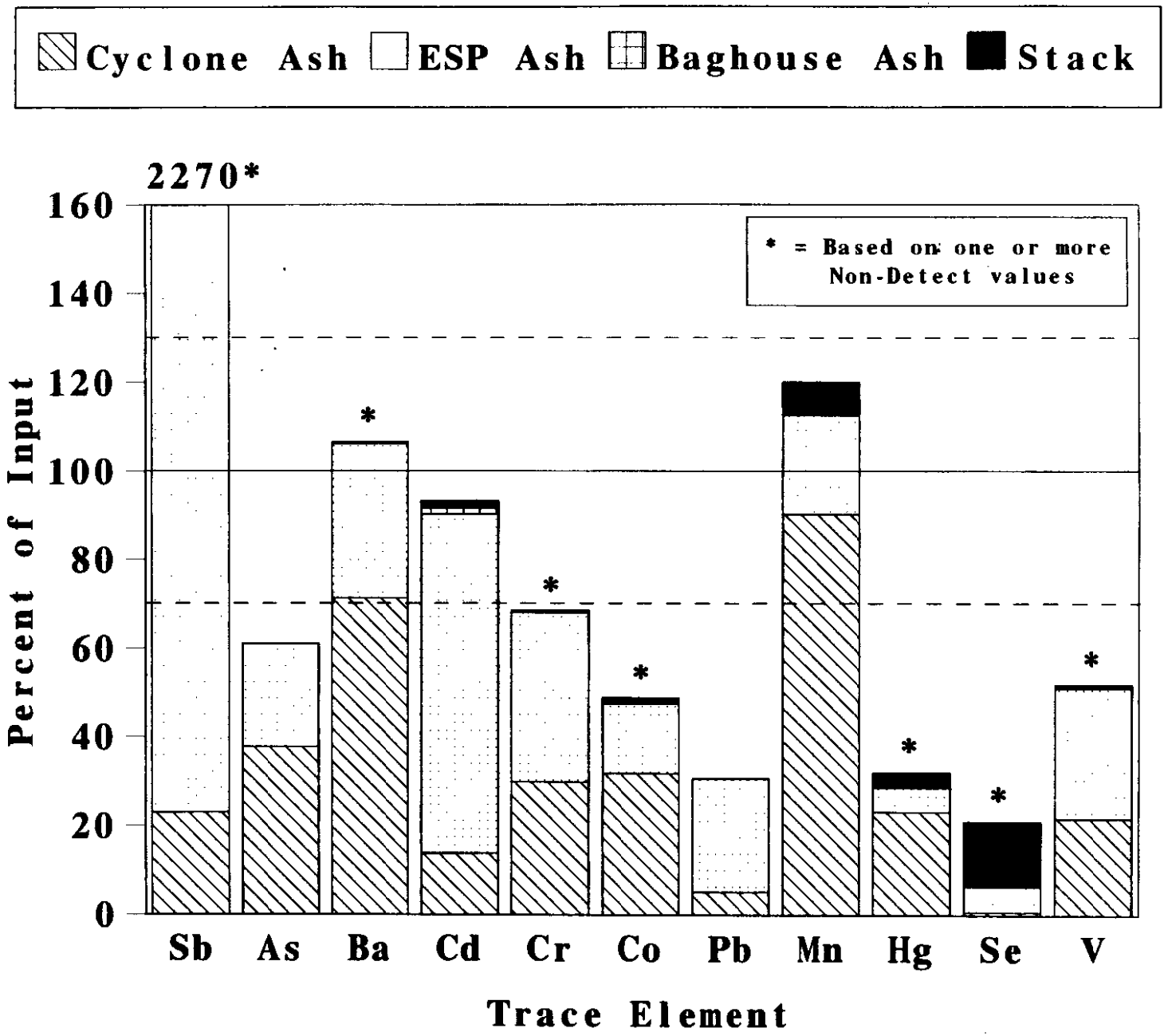

FIGURE 3.16-3. TRACE ELEMENTS IN OUTPUT STREAMS AIRPOL GSA SYSTEM, SERIES CONFIGURATION, DEMONSTRATION TESTS

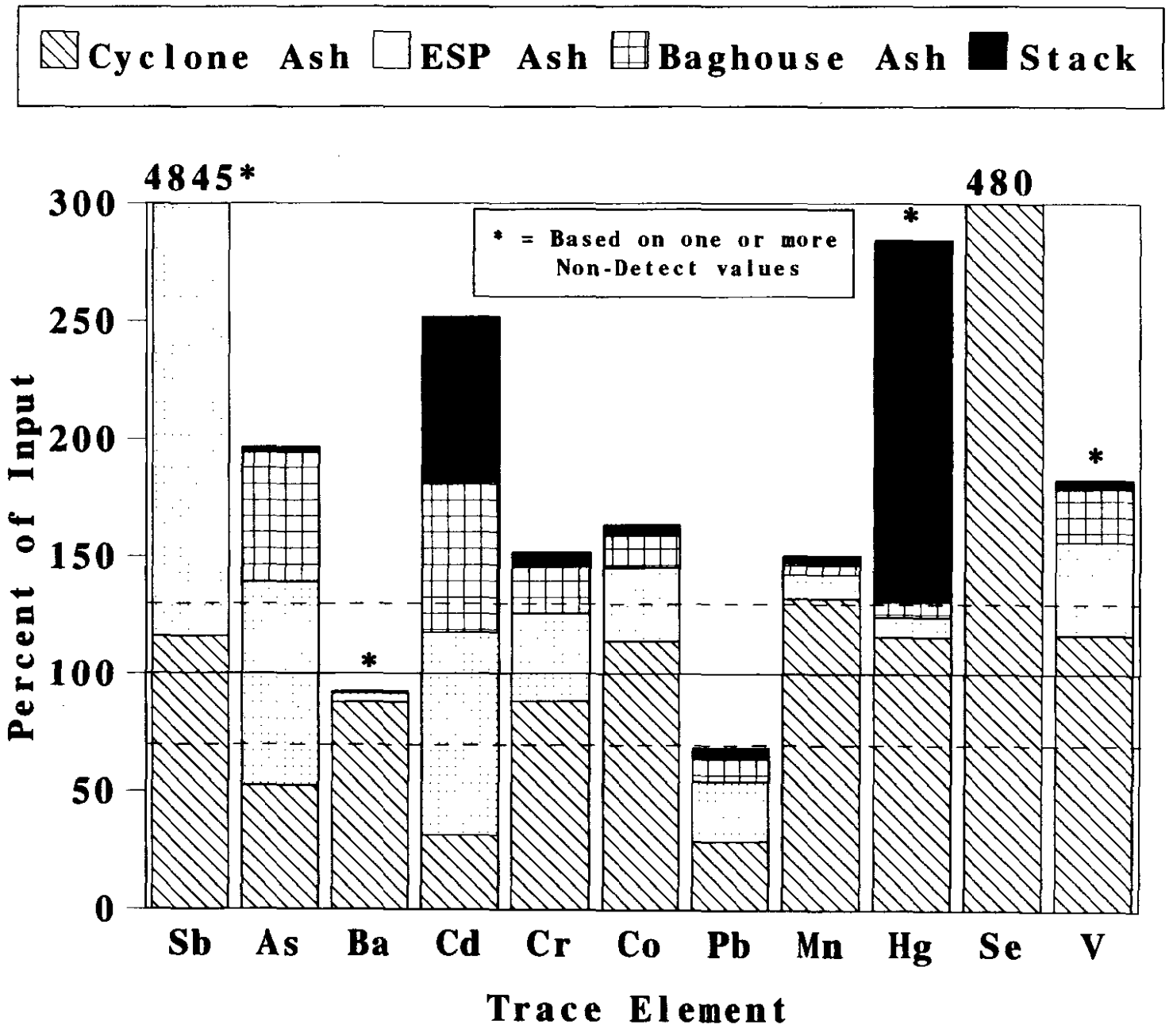

FIGURE 3.16-4. TRACE ELEMENTS IN OUTPUT STREAMS AIRPOL GSA SYSTEM, PARALLEL CONFIGURATION, BASELINE TESTS

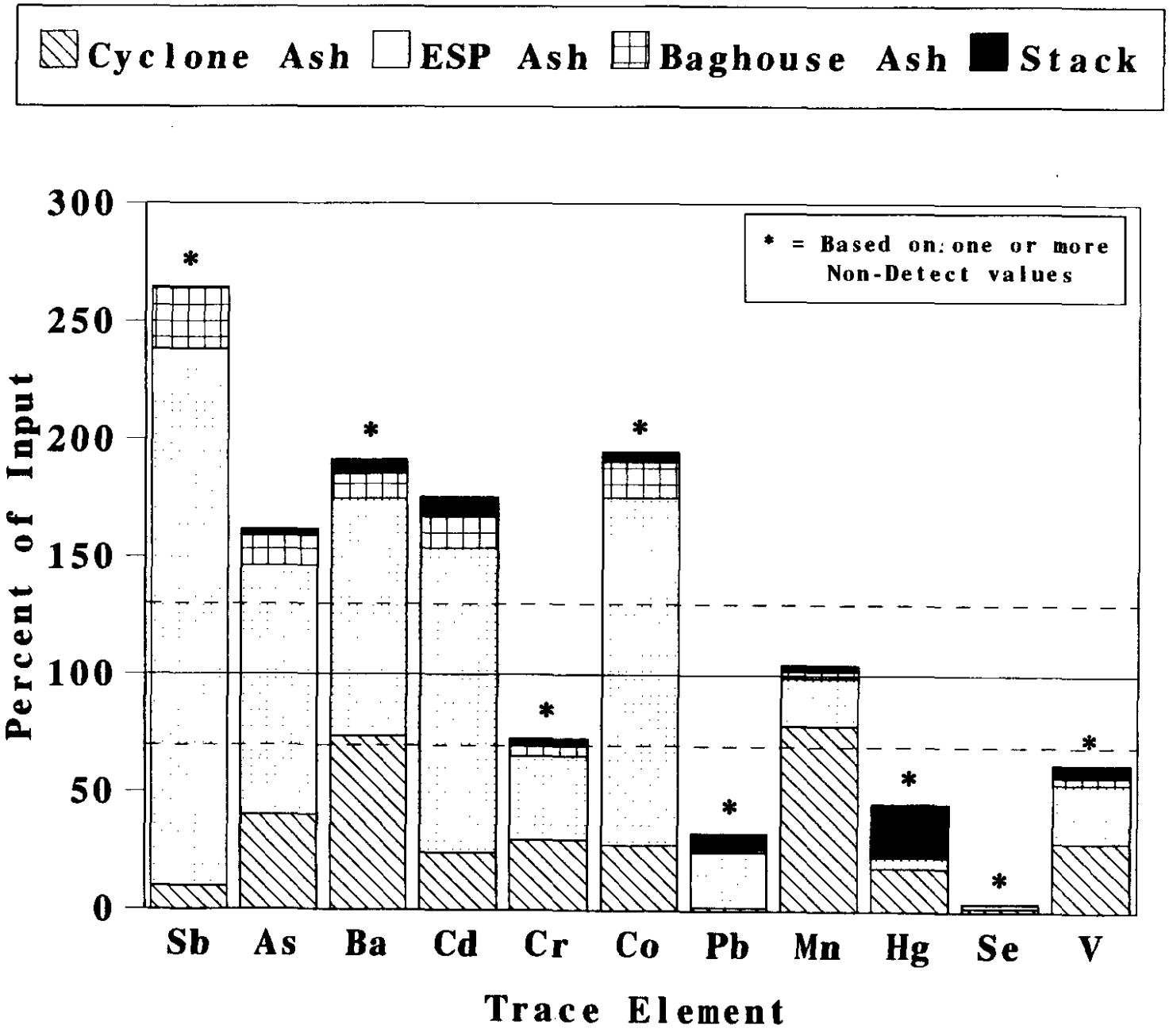

FIGURE 3.16-5. TRACE ELEMENTS IN OUTPUT STREAMS AIRPOL GSA SYSTEM, PARALLEL CONFIGURATION, DEMONSTRATION TESTS

Table 3.16-1 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant, Series Configuration, Baseline Tests

	(1) Reinjected Fly Ash	(2) GSA Slip Stream	(3) Cyclone Solids	(4) ESP In	(5) ESP Outlet
Units: lb/hr					
Antimony	ND< 0.00003 #	0.00004[B]	ND< 0.00003 #	0.00023	ND< 0.000005 #
Arsenic	0.019	0.015	0.0068	0.023	0.00043
Barium	0.048	0.058	0.034	0.113	0.0016
Cadmium	0.00012	0.00057	ND< 0.000002 #	0.00073	0.00001
Chromium	0.021	0.036	0.011	0.054	0.00050
Cobalt	0.0020	0.0047	0.0018	0.0098	0.00009
Lead	0.0068	0.011	0.00079	0.019	0.00020
Manganese	0.040	0.058	0.059	0.069	0.00068
Mercury	ND< 0.00004 #	0.00016	ND< 0.00004 #	0.00017	0.000026
Selenium	0.0014	0.011	0.0031	0.0085	0.0028
Vanadium	0.015	0.070	0.016	0.087	0.00061[B]

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples

Table 3.16-1 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant, Series Configuration, Baseline Tests, (continued)

	(6) ESP Ash	(7) Baghouse In	(8) Baghouse Ash	(9) Baghouse Out	(10) Stack
Units: lb/hr					
Antimony	ND< 0.0024	ND< 0.000002 #	ND< 0.000003 #	ND< 0.000001 #	ND< 0.000007 #
Arsenic	0.0052	0.000038	0.000006	0.000001[B]	0.00043[B]
Barium	0.018	0.00042	0.000014	ND< 0.000065 #	0.0017
Cadmium	0.00018[A]	0.000004	0.000005	0.000008	0.000023
Chromium	0.0092	0.00020	0.000008	ND< 0.000038 #	0.00053
Cobalt	0.0011	0.000040	0.000001	ND< 0.000017 #	0.00011[C]
Lead	0.0025	0.000035	0.000004	0.000010	0.00021
Manganese	0.0119	0.00017	0.000024	0.000037	0.00072
Mercury	0.000009[C]	0.000001[B]	0.0000002[A]	0.000002	0.000028
Selenium	0.00068[C]	0.00012	0.000002	0.000020	0.0028
Vanadium	0.0103[C]	ND< 0.00020 #	0.000027	ND< 0.00013 #	0.00074

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples

Table 3.16-2 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant, Series Configuration, Demonstration Tests

	(1) Reinjected Fly Ash	(2) GSA Slip Stream	(11) Lime Slurry	(12) Trim Water	(4) ESP In	(3) Cyclone Solids
Units: lb/hr						
Antimony	ND< 0.00004 #	0.00008[A]	ND< 0.00020 #	ND< 0.00001 #	0.00007[B]	ND< 0.00007 #
Arsenic	0.0276	0.0149	0.00235	ND< 0.000003 #	0.0111	0.017
Barium	0.0633	0.0139	0.00350	0.00011	0.109	0.058
Cadmium	0.00013	0.00057	0.00003	ND< 0.000002 #	0.00066	0.00010[B]
Chromium	0.0078	0.028	0.0110	ND< 0.00002 #	0.0431	0.0139
Cobalt	0.0020	0.0039	ND< 0.00086 #	ND< 0.00003 #	0.0065	0.0022
Lead	0.0084	0.0078	ND< 0.00009 #	ND< 0.000003 #	0.0131	0.00085
Manganese	0.0365	0.0308	0.0114	ND< 0.000003 #	0.0654	0.0712
Mercury	ND< 0.00004 #	0.00010	ND< 0.00024 #	ND< 0.000001 #	0.0001	ND< 0.00009 #
Selenium	0.0010	0.0069	0.0036	ND< 0.0000003 #	0.0141	ND< 0.00009 #
Vanadium	0.0119	0.0638	0.0055	ND< 0.00003 #	0.0615	0.0176

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples

Table 3.16-2 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant, Series Configuration, Demonstration Tests, (continued)

	(5) ESP Outlet	(6) ESP Ash	(7) Baghouse In	(8) Baghouse Ash	(9) Baghouse Out	(10) Stack
Units: lb/hr						
Antimony	0.00001[B]	ND< 0.0070 #	ND< 0.000002 #	ND< 0.000004 #	ND< 0.000001 #	0.000015[B]
Arsenic	0.00001	0.0104	0.000002[B]	0.000013	ND< 7.56e-07 #	0.000014[C]
Barium	ND< 0.00028 #	0.0282[A]	ND< 0.000104 #	0.000019	ND< 0.000059 #	ND< 0.000335 #
Cadmium	0.000008[A]	0.00056[A]	0.000004	0.00001	0.000004[A]	0.000012
Chromium	ND< 0.00016 #	0.0177	ND< 0.00006 #	0.000016	ND< 0.000034 #	ND< 0.000195 #
Cobalt	ND< 0.00007 #	0.0011[C]	ND< 0.000027 #	0.000002	ND< 0.000015 #	ND< 0.000086 #
Lead	0.00002[B]	0.0041[A]	0.000023	0.000006	0.000005	0.000021[B]
Manganese	0.0057	0.0176	0.00003	0.000046	0.000025	0.005753
Mercury	0.00001	ND< 0.000021 #	0.000003	4.21e-07	0.000002[A]	0.000013[A]
Selenium	0.0017	0.00066[C]	0.000002[B]	ND< 4.63e-08 #	ND< 8.23e-07 #	0.001663
Vanadium	ND< 0.00053 #	0.0238[C]	ND< 0.0002 #	0.000018[A]	ND< 0.000114 #	ND< 0.000648 #

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples

Table 3.16-3 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant Parallel Configuration, Baseline Tests

	(1) Reinjected Fly Ash	(2) GSA Slip Stream	(3) Cyclone Solids	(4) ESP In	(5) ESP Outlet
Units: lb/hr					
Antimony	ND< 0.00003 #	N/A	ND< 0.00004 #	0.00071	ND< 0.000005 #
Arsenic	0.021	N/A	0.0108	0.019	0.00047
Barium	0.050	N/A	0.044	0.031	ND< 0.00029 #
Cadmium	0.00017	N/A	0.000054[B]	0.00063	0.00008
Chromium	0.011	N/A	0.010	0.031	0.00059
Cobalt	0.0027	N/A	0.0031	0.0057	0.00011
Lead	0.0075	N/A	0.0022	0.015	0.00035
Manganese	0.031	N/A	0.041	0.027	0.00083
Mercury	ND< 0.00004 #	N/A	ND< 0.00005 #	0.00001[B]	0.000043
Selenium	0.0017	N/A	0.0058	ND< 0.00001 #	0.0012
Vanadium	0.019	N/A	0.022	0.031[A]	ND< 0.00056[B]

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples
N/A Not Analyzed

Table 3.16-3 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant Parallel Configuration, Baseline Tests, (continued)

	(6) ESP Ash	(7) Baghouse In	(8) Baghouse Ash	(9) Baghouse Out	(10) Stack
Units: lb/hr					
Antimony	ND< 0.0012 #	0.00025	ND< 0.00039 #	ND< 0.000001 #	ND< 0.000006 #
Arsenic	0.0178	0.00585	0.0113	0.000013	0.00048
Barium	0.0018[C]	0.0167	ND< 0.00012 #	ND< 0.000073 #	ND< 0.0004 #
Cadmium	0.00015	0.00009	0.00011	0.000039	0.000119
Chromium	0.0040	0.0084	0.0021	ND< 0.000042 #	0.00064
Cobalt	0.00085	0.0015	0.00037	ND< 0.000019 #	0.00012
Lead	0.0019[A]	0.0048	0.00070	0.000017	0.00037
Manganese	0.0032	0.0074	0.0016	0.000058	0.00089
Mercury	ND< 0.000003[C]	0.00002	0.000003[A]	0.000020[A]	0.000063
Selenium	0.00069[A]	0.00006[B]	0.00050	ND< 0.000001 #	0.0012
Vanadium	0.0073[B]	0.0164	0.0043	ND< 0.00014 #	ND< 0.00070[C]

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
\# Non-detectible in all samples
N/A Not Analyzed

Table 3.16-4 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant Parallel Configuration, Demonstration Tests

	(1) Reinjected Fly Ash	(2) GSA Slip Stream	(11) Limestone Slurry	(12) Trim Water	(4) ESP Inlet	(3) Cyclone Solids
Units: lb/hr						
Antimony	ND< 0.00003 #	0.00048	ND< 0.00026 #	N/A	0.0017	ND< 0.00008 #
Arsenic	0.0172	0.0220	0.0017	N/A	0.0319	0.016
Barium	0.0556	0.0049	0.0044	N/A	0.164	0.048
Cadmium	0.00014	0.00051	0.00006	N/A	0.00082	0.00018[A]
Chromium	0.0122	0.0272	0.0118	N/A	0.0427	0.0152
Cobalt	0.0028	0.0052	ND< 0.0011 #	N/A	0.0084	0.0025
Lead	0.0057	0.0101	ND< 0.00011 #	N/A	0.0212	0.00025[A]
Manganese	0.0352	0.0216	0.0174	N/A	0.0423	0.0582
Mercury	ND< 0.00004 #	0.00016	ND< 0.00032 #	N/A	0.00028	ND< 0.00010 #
Selenium	0.0015	0.00082[A]	0.0032	N/A	ND< 0.00002 #	ND< 0.00010 #
Vanadium	0.0184	0.0492	0.0071	N/A	0.0841	0.0219

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
Non-detectible in all samples
N/A Not Analyzed

Table 3.16-4 Trace Element Flow Rates, AirPol GSA, Shawnee Power Plant Parallel Configuration, Demonstration Tests, (continued)

	(5) ESP Outlet	(6) ESP Ash	(7) Baghouse Inlet	(8) Baghouse Ash	(9) Baghouse Outlet	(10) Stack
Units: lb/hr						
Antimony	ND< 0.00001 #	ND< 0.0085 #	0.00017	ND< 0.00095 #	ND< 0.000001 #	ND< 0.000006 #
Arsenic	0.0011	0.0434	0.0029	0.0053	0.000002[B]	0.0011[B]
Barium	0.0038	0.0657	0.0087	0.0069	ND< 0.00007 #	0.0038[C]
Cadmium	0.00003	0.00093	0.00004	0.00009	0.00003	0.00006
Chromium	0.0016[A]	0.0182	0.0028	0.0022	ND< 0.00004 #	0.0016[C]
Cobalt	0.00035[A]	0.0136	0.00060	0.0014	ND< 0.00002 #	0.00037[C]
Lead	0.0010	0.0037[B]	0.0011	ND< 0.00022 #	0.00001	0.0010
Manganese	0.0020	0.0152	0.0037	0.0021	0.00010	0.0021
Mercury	0.00010	ND< 0.00003 #	0.00002	0.000003 #	0.00001	0.00011
Selenium	ND< 0.000004 #	ND< 0.00009 #	ND< 0.000003 #	ND< 0.00001 #	ND< 0.0000010 #	ND< 0.000005 #
Vanadium	0.0033[A]	0.0186[C]	0.0062	0.0025[A]	ND< 0.00013 #	0.0035[C]

ND< Value shown is detection limit
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
[C] Includes five non-detect measurements (parallel sampling of two streams)
\# Non-detectible in all samples
N/A Not Analyzed

Table 3.16-5 Concentrations and Removal Efficiencies, AirPol GSA Pilot Plant, Series Tests

	Series Baseline						Series Demonstration					
	ESP Inlet, µg/dNm³	ESP Outlet, µg/dNm³	Baghouse Inlet, µg/dNm³	Baghouse Outlet, µg/dNm³	ESP Removal Efficiencies, Percent	ESP plus Baghouse Removal Efficiencies, Percent	ESP Inlet, µg/dNm³	ESP Outlet, µg/dNm³	Baghouse Inlet; µg/dNm³	Baghouse Outlet, µg/dNm³	ESP Removal Efficiencies, Percent	ESP plus Baghouse Removal Efficiencies, Percent
Antimony	2.85	ND< 0.09 #	< 0.172 #	ND< 0.095 #	89.7	89.7	0.87	0.243	ND< 0.16 #	ND< 0.079 #	84.7	95.0
Arsenic	283	7.13	3.55	ND< 0.09 #	98.7	99.98	147	0.216	0.126	ND< 0.056 #	99.96	99.99
Barium	1,370	26.5	39.1	ND< 5.22 #	98.4	99.7	1,439	ND< 4.66 #	ND< 8.60 #	ND< 4.35 #	99.6	99.7
Cadmium	8.91	0.249	0.405	0.634	97.4	94.0	8.75	0.129	0.293	0.30	98.7	97.4
Chromium	658	8.27	18.4	ND< 3.03 #	99.1	99.7	567	ND< 2.71 #	ND< 4.99 #	ND< 2.52 #	99.5	99.7
Cobalt	120	1.57	3.67	ND< 1.35 #	98.4	98.7	86.2	ND< 1.20 #	ND< 2.22 #	ND< 1.12 #	98.7	99.1
Lead	234	3.31	3.25	0.823	98.8	99.7	173	0.27	1.93	0.374	99.9	99.9
Manganese	835	11.4	15.4	2.99	99.2	99.8	862	96.7	2.48	1.85	92.4	99.9
Mercury	2.03	0.441	0.095	0.153	79.2	99.9	1.43	0.178	0.25	0.161	88.3	90.2
Selenium	103	46.9	10.9	1.59	73.1	99.1	185	28.1	0.189[a]	ND< 0.061 #	76.9	99.96
Vanadium	1,060	10.2[a]	ND<18.18 #	ND< 10.1 #	98.7	99.2	809	ND< 9.03 #	ND< 16.7 #	ND< 8.41 #	99.2	99.5

ND< Value shown is detection limit.
Of the calculations contributing to the average value shown, all include a non-detect measurement.

Table 3.16-6 Concentrations and Removal Efficiencies, AirPol GSA Pilot Plant, Parallel Tests

	Parallel Baseline						Parallel Demonstration					
	ESP Inlet, µg/dNm³	ESP Outlet, µg/dNm³	Baghouse Inlet, µg/dNm³	Baghouse Outlet, µg/dNm³	ESP Removal Efficiencies, Percent	Baghouse Removal Efficiencies, Percent	ESP Inlet, µg/dNm³	ESP Outlet, µg/dNm³	Baghouse Inlet, µg/dNm³	Baghouse Outlet, µg/dNm³	ESP Removal Efficiencies, Percent	Baghouse Removal Efficiencies, Percent
Antimony	8.61	ND< 0.09 #	23.0	ND< 0.10 #	96.6	96.7	20.1	ND< 0.09 #	13.7	ND< 0.09 #	98.8	98.7
Arsenic	237	8.23	541	0.98	98.4	99.8	388	19.2	228	0.12[B]	96.4	99.98
Barium	380	ND< 5.07 #	1,550	ND< 5.6 #	99.5	99.5	1,990	66.0	691	ND< 4.7 #	92.7	99.5
Cadmium	7.70	1.39	8.55	3.02	85	71.4	9.91	0.59	2.98	1.86	93.3	78.7
Chromium	379	10.4	781	ND< 3.3 #	98.1	99.5	519	27.3[A]	222	ND< 2.7 #	95.1	99.5
Cobalt	69.5	1.84	138	ND< 1.45 #	98.1	98.7	103	6.19[A]	47.5	ND< 1.2 #	94.3	98.9
Lead	183	6.19	442	1.29	97.3	99.5	258	17.7	86.2	0.82	92.1	99.6
Manganese	325	14.6	687	4.42	98.5	99.6	515	35.7	294	7.04	95.6	99.1
Mercury	0.13[B]	0.75	1.47	1.53[A]	62.5	32	3.35	1.74	1.84	1.02	-38.9	49.2
Selenium	ND< 0.18 #	20.5	5.94[B]	ND< 0.08 #	79.7	99.9	ND< 0.30 #	ND< 0.07 #	ND< 0.2 #	ND< 0.07 #	99.8	99.8
Vanadium	375. A	ND< 9.81[B]	1,520	ND< 10.8 #	98.8	99.1	1,020	58.5	491	ND< 9.1 #	93.4	99

ND< Value shown is detection limit.
[A] Includes one non-detect measurement
[B] Includes two non-detect measurements
Non-detectible in all samples

Table 3.16-7 Stream Temperatures, AirPol GSA System

Temperature, deg F		
	Baseline	Demonstration
GSA Inlet	290	294
ESP Outlet	243	146

SECTION 4.0 MERCURY SPECIATION

Section 4.1 Speciation Results

The following three tables summarize the test results for mercury speciation at the test facilities described in Section 3.0 of this report. Efforts are continuing to validate a method to quantitatively speciate mercury forms.

Table 4.1-1 Comparison of Mercury Measuring Techniques at Plant Stack

Plant	Concentrations, $\mu g/Nm^3$							
	Bloom Method			Method 29			Carbon Trap	HEST
	Ionic[a]	Elemental	Total	Ionic[a]	Elemental	Total	Total	Total
Baldwin	5.0	2.1	7.2	---	---	5.2		
Boswell	2.5	0.7	3.1	---	---	2.6		
Arapahoe	ND	0.06	0.07					
Burger	4.3	4.2	8.5					
Hammond	3.0	3.6	6.6					
Smith (Baseline)	6.9	1.6	8.5					
Smith (Low NO_x)	6.1	0.6	6.7					
Bailly	0.1	3.5	3.6	2.6	0.14	2.8		
Yates	0.5	2.8	3.3	1.5	1.5	3.0		
Niles				20.6	3.2	23.8		16.4
SNOX				20.6	9.7	30.3		22.8
Coal Creek				4.4	8.3	12.7		5.4
Springerville	---	---	5.9	1.4		9.6		
Cardinal						0.45	9.21	

a - Filter and probe mercury are included with ionic.

Table 4.1-2 Mercury Speciation Using the Bloom Train

	Concentrations $\mu g/Nm^3$			
	Elemental	Ionic	Filter & Probe	Total
Baldwin				
ESP Inlet	4.7	2.6	0.89	8.3
ESP Outlet	2.1	4.7	0.33	7.2
Boswell				
Baghouse Inlet	3.7	2.1	0.70	6.5
Baghouse Outlet	0.71	2.3	0.19	3.1
Arapaho				
FFDC Inlet	0.34	6.91	---	7.24
FFDC Outlet	4.16	4.32	---	8.48
Hammond				
Stack	3.6	3.0	---	6.6
Smith-Baseline				
ESP Inlet	1.7	1.9	0.12	3.8
ESP Outlet	1.6	6.9	---	8.5
Smith-Low-NO_x				
ESP Inlet	---	---	---	<0.03
ESP Outlet	0.6	6.1	0.02	6.7
Bailly				
ESP8 Inlet	1.86	4.99	---	6.85
ESP8 Outlet	3.22	4.15	---	7.37
ESP7 Outlet	2.08	4.90	---	6.98
Stack	3.46	0.09	---	3.55
Yates (CT-121)				
ESP Inlet	2.0	4.4	---	6.4
ESP Outlet	2.5	4.8	---	7.3
Stack	2.8	0.47	---	3.3

Table 4.1-3 Method 29 Mercury Speciation

Plant/Sample Point	Concentrations µg/Nm³					
	H_2O_2 Impinger	$KMnO_4$ Impinger	Probe	Filter	Filter/Probe Combined	Total
Niles						
ESP Inlet	22.5	4.2	0.9	0.7	---	28.3
ESP Outlet	20.6	3.2	0.02	0.0	---	23.8
SNO_x						
Baghouse Inlet	19.6	6.3	1.1	0.6	---	27.7
Baghouse Outlet	24.5	3.5	0.02	0.0	---	28.0
SCR Unit Outlet	26.0	4.2	0.2	0.5	---	30.9
WSA Condenser Outlet	18.9	9.7	1.7	0.02	---	30.3
Coal Creek						
ESP Inlet	4.2	9.4	0.02	0.04	---	13.6
ESP Outlet	7.6	4.3	0.02	0.0	---	11.9
Scrubber Outlet	4.4	8.3	0.0	0.0	---	12.7
Baldwin						
ESP Inlet	---	---	---	---	---	6.8
ESP Outlet	---	---	---	---	---	5.2
Boswell						
Baghouse Inlet	---	---	---	---	---	6.4
Baghouse Outlet	---	---	---	---	---	2.6
Bailly						
ESP8 Inlet	1.04	2.87	---	0.27	---	4.2
ESP8 Outlet	1.23	2.76	---	0.03	---	4.0
ESP7 Outlet	1.40	2.76	---	0.05	---	4.2
Stack	0.14	2.65	---	0.02	---	2.8
Yates						
ESP Inlet	0.35	5.1	---	---	7.1	12.5
ESP Outlet	0.98	4.6	---	---	0.13	5.7
Stack	1.5	1.5	---	---	0.006	3.0
Springerville						
SDA Inlet	3.7	---	---	---	1.4	7.4
SDA Outlet	0.37	---	---	---	3.1	11.5
Stack	1.4	---	---	---	---	9.6
Stack Diluter	2.9	0.09	---		0.1	8.0

APPENDIX - REFERENCES AND REPORT CONTENT SUMMARY

1. "A Study to Toxic Emissions from a Coal-Fired Power Plant Utilizing and ESP/Wet FGD System" by Battelle, July 1994 (Coal Creek Station)

   Volume 1: Site description, sampling, sample analysis, results, data analyses, special topics

   Volume 2: Appendices including log sheets, auditing, sampling protocol data sheets, QA/QC, analytical protocol, uncertainty analysis

2. "A Study of Toxic Emissions from a Coal-Fired Power Plant - Niles Station Boiler No. 2" by Battelle, June 1994

   Volume 1: Site description, sampling, sample analysis, results, data analyses, special reports

   Volume 2: Appendices including log sheets, auditing, sampling protocol data sheets, QA/QC, analytical protocol, uncertainty analysis

3. "A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing the **SNOX** Innovative Clean Coal Technology Demonstration" by Battelle, July 1994 (Niles Station)

   Volume 1: Site description, sampling, sample analysis, results, data analyses, special topics

   Volume 2: Appendices including log sheets, auditing, sampling protocol data sheets, QA/QC, analytical protocol, uncertainty analysis

4. "Gas Suspension Absorption (GSA) Demonstration Plant Air Toxics Characterization" by Energy and Environmental Research Corporation, September 1994 (Draft), (Shawnee Power Plant)
One Volume: Process/plant description, sampling and analytical procedures, results, mass balances, removal efficiency, emission factors, QA/QC, uncertainty analysis

5. "Assessment of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP" by Energy and Environmental Research Corporation, December 1994 (Cardinal Station)
Main Report: Site description, sample collection, sample analysis, results, data analysis, special topics
Appendix A - External Quality Assurance
Appendix B - Sampling Protocol
Appendix C - Sampling Data Sheets
Appendix D - Internal Quality Assurance
Appendix E - Analytical Protocol
Appendix F - Uncertainty Analysis
Appendix G - Gas Run Data
Appendix H - Liquid Run Data
Appendix I - Solids Run Data

6. "Characterizing Toxic Emissions from a Coal-Fired Power Plant Demonstrating the AFGD ICCT Project and a Plant Utilizing a Dry Scrubber/Baghouse System - Springerville Generating

Station Unit 2 and Dry Scrubber/Baghouse System" by Southern Research Institute, June 1994

Main Report: Site description, sampling,, sample analysis, analytical results, data analysis, special topics

Appendices: Auditing, sampling protocol bunker coal analyses, analytical protocol, QA/QC, analytical calculations, uncertainty analyses, sampling data sheets

7. "Toxic Assessment Report - Illinois Power Company Baldwin Power Station" by Roy F. Weston, Inc., July 1994

Volume I: Unit description, study design and execution, flue gas stream results, process streams, QA/QC activities

Volume II: Process operations data, detailed test results, raw test data

Volume III: Laboratory reports

Volume IV: QA/QC audit report, QC oversight report, QA/QC activities and results, equipment calibration records, sample calculations

8. "Toxics Assessment Report - Minnesota Power Company Boswell Energy Center" by Roy F. Weston, Inc., July 1994

Volume I: Unit description, study design and execution, flue gas stream results, process streams, QA/QC activities

Volume II: Process operations data, detailed test results, raw test data

Volume III: Laboratory reports

Volume IV: QA/QC audit report, QC oversight report, QA/QC activities and results, equipment calibration records, sample calculations

9. "Characterizing Toxic Emissions from a Coal-Fired Power Plant Demonstrating the AFGD ICCT Project and Utilizing a Dry Scrubber/Baghouse System - Bailly Station Units 7 and 8 and AFGD ICCT Project" by Southern Research Institute, October, 1994.

Main Report: Site description, sampling, sample analysis, analytical results, data analysis, special topics

Appendices: Auditing, sampling protocol bunker coal analyses, analytical protocol, QA/QC, analytical calculations, uncertainty analyses, sampling data sheets

10. "A Study of Hazardous Air Pollutants at the TIDD PFBC Demonstration Plant" by Radian Corporation, October 1994.

Volume I: Site description, results, data evaluation, sample calculations

Volume II: Appendices - Sample collection and pretreatment, analytical procedures, data, QA/QC results, data trend plots, equipment calibration records, field data sheets, uncertainty formulas

11. "A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP While Demonstrating the ICCT CT-121 FGD Project" by Radian Corporation, June 1994 (Plant Yates)

One Volume: Site description, results, data evaluation, sample calculations, sample collection and pretreatment, analytical procedures, detailed analytical data, sampling data, QA/QC results data trends, plots, equipment calibration records, field data sheets, uncertainty formulas

12. "Field Chemical Emissions Monitoring Project Site 115 emissions Report" by Carnot, November 1994 (Preliminary Draft)

One Volume: Site description, results, chromium and mercury speciation results, data evaluation, sample calculations, sampling and analytical concentrations, unused data, flow rates, process operation, uncertainty analyses, QA/QC, analytical and blank correction data

13. "Hazardous Air Pollution Monitoring: Demonstration of Coal Reburning for Cyclone NO_x Boiler Control" by Acurex Environmental Corporation, June 1993

    One Volume: Facility description, test plan, tests results

14. "Field Chemical Emissions Monitoring Project: site 116 Emissions Report" by Radian Corporation, July 1994 (Plant Burger)

    One Volume: Site description, results, data evaluation, special topics, sample calculations, sampling and analytical methods, process and sampling data, QA/QC data

15. "Measurement of Chemical Emissions Under the Influence of Low-NO_x Combustion Modifications" by Southern Research Institute, October 1993 (Plant Smith)

    One Volume: Site description, sampling and measurement procedures, physical characterizations, chemical analyses results, material balance data, particle size data, special topics QA/QC

16. "Field Chemical Emissions Monitoring: Overfire Air and Overfire Air/Low NO_x Burner Operation" by Southern Company Services, Inc., November 1993 (Plant Hammond)

One Volume: Site description, results, data evaluation, sample calculations, sample collection and analysis, analytical data, QA/QC results, process stream data

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Bob Wise
Governor

Stephanie R. Timmermeyer
Cabinet Secretary

PERMIT TO CONSTRUCT
AN ELECTRICAL POWER GENERATION FACILITY

IN ACCORDANCE WITH THE WEST VIRGINIA AIR POLLUTION CONTROL LAW (W. Va. Code §§22-5-1 et seq.), AND REGULATIONS PROMULGATED THEREUNDER, THE FOLLOWING PERMITTEE IS AUTHORIZED TO CONSTRUCT, SUBJECT TO THE TERMS AND CONDITIONS OF THIS PERMIT, THE SOURCE DESCRIBED BELOW.

Name of Permittee:	Longview Power, LLC
Name of Facility:	Longview Power
Permit No.:	R14-0024
Plant ID No.:	061-00134
Effective Date of Permit:	March 2, 2004
Permit Writer:	Edward Andrews
Facility Mailing Address:	1040 Great Plains Avenue Needham, MA 02492
County:	Monongalia
Nearest City or Town:	Maidsville - Cass District
UTM Coordinates:	Easting: 589.2 km Northing: 4,395.7 km Zone: 17
Directions to Exact Location:	From Morgantown, WV Route 19 west to Route 100 North to Route 53. Proceed 5.3 miles. Turn left onto Route 53/2. Access to facility is on the right.
Type of Facility or Modification:	Construction of 6,114 MMBtu/hr pulverized coal fired boiler, which is capable of generating 600 MW of electricity.

EXHIBIT
B

AS A RESULT OF GRANTING THIS PERMIT, THE SOURCE IS SUBJECT TO 45CSR30. THE TITLE V (45CSR30) APPLICATION WILL BE DUE WITHIN TWELVE (12) MONTHS AFTER THE DATE OF THE COMMENCEMENT OF THE OPERATION OR ACTIVITY (ACTIVITIES) AUTHORIZED BY THIS PERMIT, UNLESS GRANTED A DEFERRAL OR EXEMPTION BY THE SECRETARY FROM SUCH FILING DEADLINE PURSUANT TO A WRITTEN REQUEST FROM THE PERMITTEE.

IN ACCORDANCE WITH THE PERMIT APPLICATION AND ITS AMENDMENTS, THIS PERMIT IS LIMITED AS FOLLOWS:

A. SPECIFIC REQUIREMENTS

1. The following conditions and requirements are specific to the PC Boiler (ID #SB1):

   a. The hourly heat input of the PC Boiler shall not exceed 6,114 million British Thermal Units (MMBtu) per hour.

   b. The annual heat input of the PC Boiler shall not exceed 53,558,640 MMBtu per rolling 12-month total.

2. Emissions of nitrogen oxides (NO_x) shall be controlled with the use of low NO_x burners and selective catalytic reduction control technologies. NO_x emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 489 lb/hr (0.08 lb/MMBtu) based on a 24-hour rolling average.

   a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 40 CFR 60.8.

   b. Continuous compliance with this emission limit shall be determined by Continuous Emission Monitors (CEMs) data. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for NO_x from the PC Boiler.

3. Emissions of nitrogen oxides (NO_x) shall be controlled with the use of low NO_x burners and selective catalytic reduction control technologies. NO_x emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 428 lb/hr (0.07 lb/MMBtu) based on a 30-day rolling average.

   a. Continuous compliance with this emission limit shall be determined by Continuous Emission Monitors (CEMs) data. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for NO_x from the PC Boiler.

4. Emissions of nitrogen oxides (NO_x) shall be controlled with the use of low NO_x burners and selective catalytic reduction control technologies. NO_x emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 397 lb/hr (0.065 lb/MMBtu) based on a calendar year.

a. Continuous compliance with this emission limit shall be determined by Continuous Emission Monitors (CEMs) data. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for NO_x from the PC Boiler.

5. Emissions of sulfur dioxides (SO_2) shall be controlled with the use of a wet flue gas desulfurization control technology. SO_2 emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 917 lb/hr (0.15lb/MMBtu) based on a three-hour rolling average.

   a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 40 CFR 60.8.

   b. Continuous compliance with this emission limit shall be performed by CEMs. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for SO_2 from the PC Boiler.

6. Emissions of sulfur dioxides (SO_2) shall be controlled with the use of a wet flue gas desulfurization control technology. SO_2 emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 734 lb/hr (0.12 lb/MMBtu) based on a 24-hour rolling average.

   a. Continuous compliance with this emission limit shall be performed by CEMs. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for SO_2 from the PC Boiler.

   b. The permittee shall install CEMs to measure SO_2 emissions at the inlet and outlet of the WFGD control device (ID no. CB3) in accordance with 40 CFR 60.47a.

7. Emissions of sulfur dioxides (SO_2) shall be controlled with the use of a wet flue gas desulfurization control technology. SO_2 emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 581 lb/hr (0.095 lb/MMBtu) based on a calendar year and 2,417 tons per calendar year.

   a. Continuous compliance with this emission limit shall be performed by CEMs. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of 40 CFR 60.13 and 40 CFR 75 for SO_2 from the PC Boiler.

b. The permittee shall install CEMs to measure SO_2 emissions at the inlet and outlet of the WFGD control device (ID no. CB3) in accordance with 40 CFR 60.47a.

8. Emissions of particulate matter (PM) shall be controlled with fabric filter control technology. PM emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 110 lb/hr (0.018 lb/MMBtu) based on a six-hour rolling average.

   a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 40 CFR 60.8.

   b. Continuous compliance with this emission limit shall be performed by CEMs. The permittee shall install, calibrate, operate and maintain CEMs in accordance with 40 CFR 60 and Performance Specification 11 (PS-11).

   c. The permittee shall demonstrate on-going compliance with this limit by conducting periodic testing every three years from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 40 CFR 60.8.

9. Emissions of particulate matter less than ten microns (PM-10) shall be controlled with fabric filter control technology. PM-10 (includes filterable and condensables other than water) emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 110 lb/hr (0.018 lb/MMBtu) based on a six-hour rolling average.

   a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Methods 201 or 201A in conjunction with U.S. EPA Test Method 202 or another test method approved by the Director.

   b. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Methods 201 or 201A in conjunction with U.S. EPA Test Method 202 or another test method approved by the Director.

c. All compliance demonstrations for this limit shall, at a minimum, consist of three - two hour test runs.

10. Emissions of carbon monoxide (CO) shall be controlled with the use of good combustion practices control technology. CO emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 673 lb/hr (0.11 lb/MMBtu) based on a three-hour rolling average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 10B or another test method approved by the Director.
    b. Continuous compliance with this emission limit shall be performed by CEMs. The permittee shall install, calibrate, operate and maintain CEMs, in accordance with the requirements of PS-4, PS-4A or PS-4B of Appendix B of 40 CFR 60 and the Quality Assurance Procedures of Appendix F of 40 CFR 60 for CO from the PC Boiler.

11. Emissions of volatile organic compounds (VOC) shall be controlled with the use of good combustion practices control technology. VOC emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 24.5 lb/hr (0.004 lb/MMBtu) based on a three-hour rolling average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 18 or another test method approved by the Director.

    b. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 18 or another test method approved by the Director.

    c. Continuous compliance with this emission limit shall be determined by using the data generated by CEMs under Paragraph A.10.b for CO as a surrogate for VOC. The permittee shall establish through testing the relationship between CO emissions and VOC emissions. A violation based on the CEMs data for CO and the relationship between CO and VOCs constitutes a violation of this emission limit for VOC. The permittee shall have the option to perform emission testing to verify the relationship between CO and VOC if the CEMs data for CO indicates a violation of the VOC emission limit. Testing performed after the violation to determine

whether the underlying relationship between CO and VOC has changed shall not be an absolute defense to the violation.

12. Emissions of sulfuric acid mist (H_2SO_4) shall be controlled with the use of dry sorbent injection in conjunction with fabric filter control technology. H_2SO_4 emissions emitted to the atmosphere from the PC Boiler Stack (EP #EB1) shall not exceed 45.8 lb/hr (0.0075 lb/MMBtu) based on a 3-hour rolling average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 8 or another test method approved by the Director.

    b. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 8 or another test method approved by the Director.

    c. Continuous compliance with this emission limit shall be determined by using the data generated by CEMs under Paragraph A.5.b for SO_2 as a surrogate for H_2SO_4. The permittee shall establish through testing the relationship between SO_2 emissions and H_2SO_4 emissions. A violation based on the CEMs data for SO_2 and the relationship between SO_2 and H_2SO_4 constitutes a violation of this emission limit for H_2SO_4. The permittee shall have the option to perform emission testing to verify the relationship between SO_2 and H_2SO_4 if the CEMs data for SO_2 indicates a violation of the H_2SO_4 emission limit. Testing performed after the violation to determine whether the underlying relationship between H_2SO_4 and SO_2 has changed shall not be an absolute defense to the violation.

13. Emissions of Mercury (Hg) from the PC Boiler Stack shall not exceed 1.46×10^{-2} lb/hr based on a three-hour average and 6.38×10^{-2} TPY based on 12 month rolling average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 29 or the draft ASTM Z65907, "Standard Method for Both Speciated and Elemental Mercury Determination" or another Test Method approved by the Director.

b. Continuous compliance with this emission limit shall be determined by Hg CEMs. The permittee shall install, calibrate, operate and maintain CEMs in accordance with 40 CFR 60.

14. Emissions of Beryllium (Be) from the PC Boiler Stack shall not exceed 5.46×10^{-3} lb/hr based on a three-hour average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 29 or another Test Method approved by the Director.

    b. The permittee shall demonstrate compliance with this emission limit by determining the Be content of the coal consumed by the PC Boiler on a biweekly basis. The permittee shall keep record of this analysis on site and utilize this content with the results of the most recent testing to determine the Be emissions during the respective two week period for which the coal sample was taken.

    c. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 29 or another Test Method approved by the Director.

15. Emissions of Lead (Pb) from the PC Boiler Stack shall not exceed 0.109 lb/hr based on a three-hour average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 29 or another Test Method approved by the Director.

    b. The permittee shall demonstrate compliance with this emission limit by determining the Pb content of the coal consumed by the PC Boiler on a biweekly basis. The permittee shall keep record of this analysis on site and utilize this content with the results of the most recent testing to determine the Pb emissions during the respective two week period for which the coal sample was taken.

    c. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections

of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 29 or another Test Method approved by the Director.

16. Emissions of hydrochloric acid (HCL) shall be controlled with the use of dry sorbent injection in conjunction with fabric filter control technology. Emissions of HCL from the PC Boiler Stack shall not exceed 2.14×10^{-3} lb/hr (1.00×10^{-5} lb/MMBtu) based on a three-hour average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 26A or another test method approved by the Director.

    b. The permittee shall determine the chlorine content of the coal consumed by the PC Boiler on a biweekly basis. The permittee shall keep record of this analysis on site and utilize this content with the results of the most recent testing to determine the HCL emissions during the respective two week period for which the coal sample was taken.

    c. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 26A or another Test Method approved by the Director.

17. Emissions of hydrofluoric acid (HF) shall be controlled with the use of dry sorbent injection in conjunction with fabric filter control technology. Emissions of HF from the PC Boiler Stack shall not exceed 2.14×10^{-3} lb/hr (1.00×10^{-5} lb/MMBtu) based on a three-hour average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 26A or another test method approved by the Director.

    b. The permittee shall determine the fluoride content of the coal consumed by the PC Boiler on a biweekly basis. The permittee shall keep record of this analysis on site and utilize this content with the results of the most recent testing to determine the HF emissions during the respective two week period for which the coal sample was taken.

    c. The permittee shall demonstrate compliance with this limit by conducting periodic testing annually from the date of the initial compliance test. This testing shall be conducted in accordance with the appropriate subsections

of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 26A or another Test Method approved by the Director.

18. Visible emissions from the PC Boiler shall not exceed 10% opacity on a 6-minute averaging period.

    a. The permittee shall demonstrate compliance with this standard by complying with the applicable opacity monitoring requirements of 40 CFR 60.46b and 45SCR2 or another test method approved by the Director.

19. The stack height for the PC Boiler shall be constructed at a height of 554 feet above ground elevation.

20. For the purposes of mitigating acid deposition and visibility impacts into the Dolly Sods Wilderness Area, James River Face Wilderness Area, Otter Creek Wilderness Area, and Shenandoah National Park, (collectively the Class I Areas), the permittee shall obtain and permanently retire sulfur dioxide allowances in accordance with the following.

    a. The required number of sulfur dioxide allowances for the respective calendar year shall be determined by the actual sulfur dioxide emission, in tons, emitted from the PC boiler during each calendar year plus 10% and multiplied by the corresponding offset ratio as defined in paragraph b of this condition.

    b. Acceptable sulfur dioxide allowances under this condition shall be from facilities that were allocated sulfur dioxide allowances under 40 CFR 73 and that are located within one of the four quadrants as defined in the following table:

Quadrant	Northeast	Northwest	Southeast	Southwest
Offset Ratio	1:4	1:1	1:4	1:1
	Longitude/Latitude	Longitude/Latitude	Longitude/Latitude	Longitude/Latitude
Northeast Corner	-77.528845/ 40.100689	-79.312228/ 40.119496	-77.73267/ 38.570665	-79.338651/ 38.603830
Northwest Corner	-79.312228/ 40.119496	-80.555022/ 40.151887	-79.338651/ 38.603830	-80.944637/ 38.628678
Southeast Corner	-77.73267/ 38.570665	-79.338651/ 38.603830	-77.671583/ 37.077938	-79393612/ 37.088164
Southwest Corner	-79.338651/ 38.603830	-80.944637/ 38.628678	-79393612/ 37.088164	-80.573361/ 37.123911

c. The vintage year of the allowances shall correspond to the calendar year that is being mitigated.

d. The permittee shall transfer these allowances into an account in the Allowance Tracking System administered by with U.S. EPA for the Acid Rain Program, to be identified by the Director. These retired allowances can never be used to meet any compliance requirement under the Clean Air Act or any State Implementation Plan.

e. The permittee shall submit a report to the Director no later than 60 days after the end of each calendar year, which shall contain the amount of sulfur dioxide emitted; the amount, facility, location of facility, vintage year of allowances retired, proof that allowances have been transferred into account identified by the Director and any applicable serial or other identification associated with the retired allowances.

f. At any time, but after at least 30 days notice to the public and the Federal Land Managers, the Director may approve an alternative mitigation plan in lieu of this condition. At a minimum, such a plan shall result in actual sulfur dioxide reductions from an existing stationary source(s) within one of the four quadrants as defined in b of this condition of at least 2,142 tons per year multiplied by the corresponding offset ratio. Such reductions must be practically enforceable, permanent, and quantifiable, and must be created after March 2, 2004. The reductions must result in the same or greater reduction in acid deposition and visibility impacts to the Class I Areas as the purchase of allowances as set forth in Paragraphs A.20.a through A.20.e herein.

21. The PC Boiler is subject to state rules 45 CSR 2, 45 CSR 26 and 45 CSR 33. The permittee shall comply with the applicable requirements from these rules (i.e. monitoring, testing, record keeping, and reporting requirements).

22. The PC Boiler is subject to 40 CFR 60 Subpart Da. The permittee shall comply with the applicable requirements from this regulation (i.e. monitoring, testing, record keeping, and reporting requirements).

23. The following conditions and requirements are specific to the Auxiliary Boiler (ID #SX1):

    a. The hourly heat input of the Auxiliary Boiler shall not exceed 225 million British Thermal Units (MMBtu) per hour.

i. The permittee shall monitor and record the amount of fuel consumed on a daily basis. Using the amount of fuel consumed, the appropriate Higher Heating Value (HHV) of the fuel and appropriate engineering calculations, the permittee shall determine the hourly heat input of the Auxiliary Boiler on a daily basis.

b. The permittee shall not operate the Auxiliary Boiler greater than 3,000 hours in a 12-month rolling period.

i. The permittee shall keep monthly records of hours the auxiliary boiler operated and a 12-month rolling total.

c. The Auxiliary Boiler shall not consume more than 675 million cubic feet of pipeline quality natural gas on a annual basis.

i. The permittee shall keep monthly records of amount of natural gas consume by the auxiliary boiler and a 12-month rolling total.

d. The permittee shall perform annual maintenance of the Auxiliary Boiler and shall keep records of this maintenance.

24. Emissions of nitrogen oxides (NO_x) shall be controlled with the use of low NO_x burners and good combustion practices control technologies. NO_x emissions emitted to the atmosphere from the Auxiliary Boiler Stack (EP #EX1) shall not exceed 22.1 lb/hr (0.098 lb/MMBtu) based on a three-hour average.

a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 40 CFR 60.8.

25. Emissions of SO_2 shall be controlled with the use of clean fuels (i.e. natural gas) control technology. SO_2 emissions emitted to the atmosphere from the Auxiliary Boiler Stack (EP #EX1) shall not exceed 0.004 lb/hr ($1.8x10^{-5}$ lb/MMBtu) based on a three-hour average.

a. The auxiliary boiler shall not consume any natural gas with a sulfur content greater than 0.15 grains per 100 cubic of natural gas. The permittee shall keep annual records of the sulfur content of the natural gas consumed.

26. PM and PM-10 emissions emitted to the atmosphere from the Auxiliary Boiler Stack (EP #EX1) shall not exceed 0.50 lb/hr ($2.22x10^{-3}$ lb/MMBtu) based on a six-hour average.

a. Initial compliance with this PM emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and 45CSR2.

27. CO emissions emitted to the atmosphere from the Auxiliary Boiler Stack (EP #EX1) shall not exceed 9 lb/hr (0.04 lb/MMBtu) based on a three-hour average.

    a. Initial compliance with this emission limit shall be performed by the permittee through compliance testing in accordance with the appropriate subsections of **Section B. Other Requirements** of this permit and U.S. EPA Test Method 10B or another test method approved by the Director.

28. VOC emissions emitted to the atmosphere from the Auxiliary Boiler Stack (EP #EX1) shall not exceed 1.21 lb/hr (5.4×10^{-3} lb/MMBtu) based on a three-hour average.

29. Visible emissions from the PC Boiler shall not exceed 10% opacity on a 6-minute averaging period.

30. The Auxiliary Boiler is subject to state rules 45 CSR 2 and 45 CSR 10. The permittee shall comply with the applicable requirements from these rules (i.e. monitoring, testing, record keeping, and reporting requirements).

31. The Auxiliary Boiler is subject to 40 CFR 60 Subpart Db. The permittee shall comply with the applicable requirements from this regulation (i.e. monitoring, testing, record keeping, and reporting requirements).

32. The following conditions and requirements are specific to the internal combustion engines powering the emergency generator (ID #SG1) and fire pump (ID #SP1):

    a. The hours of operation for the engines of the emergency generator and fire pump shall be limited to 500 hours per rolling 12 month time period for each engine.

        i. The permittee shall keep monthly records of hours of operation and a 12-month rolling total.

    b. The sulfur content of the fuel used in the emergency generator and fire pump engines shall not exceed 0.05% sulfur by weight.

    c. The emergency generator engine (ID #SG1) shall not consume more than 14,750 gallons of fuel on an annual basis.

d. The fire pump engine (ID #SP1) shall not consume more than 7,380 gallons of fuel on an annual basis.

e. Emissions from the emergency generator and fire pump engines shall not exceed the following limits:

Table 1 - Emission Limits for the Emergency Generator and Fire Pump Engines

Pollutants	Emergency Generator		Fire Pump	
	lb/hr	tons per year*	lb/hr	tons per year*
SO_2	6.5	1.6	3.3	0.825
PM_{10}	1.13	0.28	0.56	0.14
CO	8.85	2.21	4.43	1.11
NO_X	20.9	5.23	10.5	2.6
VOC	1.21	0.30	0.64	0.16

* Based on operating 500 hours per year

f. The permittee shall perform annual maintenance of the emergency generator and fire pump engine and shall keep records of this maintenance.

33. The conditions and requirements in the following subdivisions are specific to the mechanical draft cooling tower (ID #ST-1):

a. Emissions of PM and PM-10 shall be controlled with a 0.002% drift eliminator or an equivalent control technology. PM-10 emissions emitted to the atmosphere from the Cooling Tower (EP #ET1) shall not exceed 0.90 lb/hr and 3.9 TPY.

i. For the purpose of determining compliance with this emission limit, the permittee shall monitor the flow and the concentration of total dissolved solids contained in the circulating water in the cooling tower on a daily basis. The permittee shall determine the PM-10 emissions using the current version of AP-42 for mechanical draft cooling towers.

ii. The permittee shall perform an initial drift test and periodic drift testing once every five years thereafter.

34. The following conditions and requirements are specific to the coal handling operations:

a. The coal transferred through the facility shall not exceed the maximum material throughputs as shown in Table 2 - "Coal Transfer Limits" of this permit.

b. Pollution control mechanisms shall be installed and maintained on all material transfer points in accordance to Table 2 - "Coal Transfer Limits" of this permit.

Table 2 - Coal Transfer Limits

Transfer Point		Pollution Control Device	Maximum Coal Throughput	
ID	Description		Tons/Hour	Tons/Year
C-1	Truck Dump to Hopper/Reclaim Feeder	Wind screens w/dust suppression	1,000	2,365,200
C-2	Reclaim Feeders to Belt	Full Enclosure w/dust suppression	1,000	2,365,200
C-3	Belt to Pile Feeder Belt	Full Enclosure w/dust suppression	1,000	2,365,200
C-4	Belt to Coal Pile	Dust Suppression	1,000	2,365,200
C-6	Coal Reclaim Feeder	Full Enclosure w/dust suppression	600	2,365,200
C-7	Coal Reclaim Feeder	Full Enclosure w/dust suppression	600	2,365,200
C-8	Reclaim Feeder to Belt	Full Enclosure	600	2,365,200
C-9	Reclaim Feeder to Belt	Full Enclosure	600	2,365,200
C-10	Belt Transfer to Surge Bin	Full Enclosure w/dust suppression	600	2,365,200
C-11	Belt Transfer to Surge Bin	Full Enclosure w/dust suppression	600	2,365,200
C-12	Belt Transfer to Surge Bin	Full Enclosure w/dust suppression	600	2,365,200
C-15	Crusher Discharge to Belt	Full Enclosure	600	2,365,200
C-16	Crusher Discharge to Belt	Full Enclosure	600	2,365,200
C-17	Belt Transfer to Silo Feed Belt	Full Enclosure w/dust suppression	600	2,365,200
C-18	Belt Transfer to Silo Feed Belt	Full Enclosure w/dust suppression	600	2,365,200
C-19	Belt Transfer to Silo Feed Belt	Full Enclosure w/dust suppression	600	2,365,200

Transfer Point		Pollution Control Device	Maximum Coal Throughput	
ID	Description		Tons/Hour	Tons/Year
C-20	Belt Transfer to Silo Feed Belt	Full Enclosure w/dust suppression	600	2,365,200
C-22	Crusher Bypass to Belt	Full Enclosure	600	2,365,200
C-23	Crusher Bypass to Belt	Full Enclosure	600	2,365,200

c. Visible emissions from the coal crushers, conveying equipment and coal storage silos shall not exceed 20% opacity on a 6-minute averaging period.

   i. The permittee shall conduct periodic compliance testing on a monthly basis in accordance with U.S. EPA Method 22 for the purpose of determinating visible emissions from the coal crushers, conveying equipment and coal storage silos. Should the results of a periodic compliance test reveal that visible emissions are being emitted, the permittee has 24-hours from conducting Method 22 to conduct a Method 9 test to determine compliance with the emission limit in A.34.e of this permit.

d. The open stockpile SC-5 shall be limited to a maximum storage capacity of 120,000 tons of coal.

e. The two coal crushers (SC-14 & SC-15) shall not exceed the maximum processing rate of 600 tons per hour and 2,265,200 TPY for each crusher.

f. Emissions of PM and PM-10 from the coal crushers (SC-13 & SC-14) shall be controlled by a full enclosure with a dust suppression at the inlet of each surge bin for each respective crusher. PM emissions from each crusher shall not exceed 0.04 lb/hr and 0.09 TPY. PM-10 emissions from each crusher shall not exceed 0.02 lb/hr and 0.04 TPY.

g. The six (6) coal storage silos (ID #SC-21) shall be enclosed and vent to dust collector CC-21.

   i. Emissions of PM from dust collector CC-21 emitted to the atmosphere at emission point EC-21 shall not exceed 0.34 lb/hr and 1.35 TPY.

   ii. Emissions of PM-10 from dust collector CC-21 emitted to the atmosphere at emission point EC-21 shall not exceed 0.29 lb/hr and 1.15 TPY.

h. For the purposes of demonstrating compliance with the requirements in this subsection, the permittee shall monitor and record the daily amount of coal delivered to this facility.

i. The equipment and activities associated with the coal handling operation are subject to State rule 45 CSR 2. The permittee shall comply with the applicable requirements of this rule (i.e. monitoring, testing, record keeping, and reporting requirements).

j. The equipment associated with the coal handling operation is subject to 40 CFR 60 Subpart Y. The permittee shall comply with all applicable requirements from this regulation (i.e. monitoring, testing, record keeping, and reporting requirements).

35. The following conditions and requirements are specific to the limestone handling operations:

a. The material (limestone) transferred through the facility shall not exceed the maximum material throughputs as shown in Table 3 - "Limestone Handling Transfer Limits" on of this permit.

b. Pollution control mechanisms/measures shall be installed and maintained on all material transfer points in accordance with Table 3 - "Limestone Handling Transfer Limits" of this permit.

Table 3 - Limestone Handling Transfer Limits

Transfer Point		Pollution Control Device	Maximum Throughput	
ID	Description		Tons/Hour	Tons/Year
L-1	Truck Dump to Limestone Hopper Feeder	Partial Enclosure with dust suppression	150	750,075
L-2	Feeder Transfer to Bucket Elevator	Full Enclosure w/dust suppression	150	750,075
L-3	Bucket Elevator Discharge to Pile Tripper Belt	Full Enclosure w/dust suppression	150	750,075
L-4	Belt Transfer to Limestone Pile	Partial Enclosure and Telescopic Chute	150	750,075
L-6	Reclaim Transfer to Reclaim Hopper/Belt	Partial Enclosure	150	750,075
L-7	Reclaim Belt to Reclaim Conveyor	Full Enclosure w/dust suppression	150	750,075
L-8	Reclaim Conveyor to Storage Conveyor	Partial Enclosure w/dust suppression	150	750,075
L-9	Bucket Elevator Discharge to Conveyor	Partial Enclosure w/dust suppression	150	750,075

Transfer Point		Pollution Control Device	Maximum Throughput	
ID	Description		Tons/Hour	Tons/Year
L-10	Conveyor to Storage Conveyor	Partial Enclosure w/dust suppression	150	750,075
L-12	Silo Drop to Weigh Feeder	Full Enclosure	150	750,075
L-13	Ball Mill	Partial Enclosure	150	750,075

c. Stockpile L-5 shall be limited to a maximum storage capacity of 13,680 tons of limestone.

d. Stockpile L-5 shall be located in an A-frame enclosure with a roof and partial walls.

e. The limestone day silo (SL-11) shall be enclosed and vent to a dust collector (EL-11).

i. PM from limestone day silo vented to the atmosphere at emission point EL-11 shall not exceed 0.34 lb/hr based on a three-hour averaging period and 0.86 TPY.

ii. PM-10 from limestone day silo vented to the atmosphere at emission point EL-11 shall not exceed 0.29 lb/hr based on a three-hour averaging period and 0.73 TPY.

iii. Visible emissions from emission point EL-11 shall not exceed 7% opacity on a six-minute averaging period.

iv. The permittee shall conduct initial compliance testing in accordance with 40 CFR 60.08 for the purpose of demonstrating compliance with the emission limits in A.35.e.i and A.35.e.iii of this permit.

v. The permittee shall conduct periodic compliance testing on a monthly basis in accordance with U.S. EPA Method 22 for the purpose of determinating visible emissions from emission point EL-11. Should the results of a periodic compliance test reveal that visible emissions are being emitted, the permittee has 24-hours from conducting Method 22 to conduct a Method 9 test to determine compliance with the emission limit in A.35.e.iii of this permit.

vi. The permittee shall maintain records of these compliance tests on site for a period of five (5) years.

f. The equipment associated with the limestone handling operation is subject to 40 CFR 60 Subpart OOO. The permittee shall comply with all applicable requirements from this regulation (i.e. monitoring, testing, record keeping, and reporting requirements).

36. The following conditions and requirements are specific to the ash handling operations:

a. The permittee shall use a pressurized system to transfer all fly ash.

b. The permittee shall install, operate, and maintain a bin exhaust filter to control PM emissions from the fly ash storage (CA-1).

c. The bottom ash storage pile SA-7 shall be limited to a maximum storage capacity of 1,170 tons of bottom ash.

d. The gypsum storage pile SG-1 shall be limited to a maximum storage capacity of 13,680 tons of gypsum.

37. Fugitive dust control measures as proposed in Permit Applications R14-0024 shall be installed, maintained, and operated in such a manner as to minimize dust generation and atmospheric entrainment pursuant to Section 5 of 45 CSR 2. Such measures shall include, but not be limited to, the following:

a. Water spray systems for the purpose of fugitive particulate dust control shall be designed, installed, operated, and maintained so as to minimize the generation of fugitive particulate emissions from the wind erosion of stockpiles.

A properly designed, installed, and maintained winterization system on each of the water spray systems shall be in place so to functionally maintain all fugitive particulate dust control during periods when ambient temperature falls to or below 32 degrees Fahrenheit.

b. The permittee shall maintain a fixed water spray system and/or a water truck on site at the facility and in good operating condition, and shall utilize same to apply water, or a mixture of water and an environmentally acceptable dust control additive, hereinafter referred to as solution, as often as is necessary in order to minimize the atmospheric entrainment of fugitive particulate emissions that may be generated from haul roads and other work areas where mobile equipment is used.

The spray bar shall be equipped with commercially available spray nozzles, of sufficient size and number, so as to provide adequate coverage to the surface being treated.

The pump delivering the water, or solution shall be of sufficient size and capacity so as to be capable of delivering to the spray nozzle(s) an adequate quantity of water, or solution, and at a sufficient pressure.

c. The permittee shall maintain and operated as need to minimize fugitive particulate matter from haul roads a street sweeper or other mobile equipment designed to remove debris (road dust) from paved plant roads. This activity shall be conducted daily to minimize fugitive particulate matter from paved plant roadways.

d. All belt conveyors shall be at a minimum partially enclosed.

38. The permittee shall construct and maintain an industrial fence around this permitted facility as defined in the March 3, 2003 submittal of the Air Quality Modeling Analysis Report. This industrial fence shall be constructed in such a manner to reasonably prevent the public from accessing this permitted facility.

39. All roadways at the permitted facility shall be paved, and maintained in such a way to minimize fugitive particulate matter emissions.

40. Notwithstanding the specific emission limits of Hazardous Air Pollutants (HAPs) in this permit, the facility wide total emissions to the atmosphere of HAPs as defined by Section 112(b) of the 1990 Clear Air Act Amendments shall be less than 10 TPY of any single HAP and less than 25 TPY of combined total of HAPs from the facility.

a. The permittee shall on a monthly basis determine and keep record of the total amount of HAPs emitted from the facility during the past year on a rolling 12-month total basis. Records of this determination shall be on a speciated HAP basis and summing the total amount of HAP emitted during the previous 12-months. All records used to determine the amount of HAPs emitted must include but not be limited to sample calculations and collected data (i.e. fuel consumption, hours operated).

B. OTHER REQUIREMENTS

1. In accordance with 45CSR30 - "Operating Permit Program", enclosed with this permit is a Certified Emissions Statement (CES) Invoice, from the date of initial startup through the following June 30. Said invoice and the appropriate fee shall

be submitted to this office no later than 30 days prior to the date of initial startup. For any startup date other than July 1, the permittee shall pay a fee or prorated fee in accordance with the Section 4.5 of 45CSR22. A copy of this schedule may be found attached to the Certified Emissions Statement (CES) Invoice.

2. The permittee shall comply with all applicable provisions of 45CSR2, 45CSR10, 45CSR11, 45CSR14, 45CSR16, 45CSR26, 45CSR30, 45CSR33, 40 CFR 60 - Subpart Da, 40 CFR 60 - Subpart Db, 40 CFR 60 - Subpart Y, and 40 CFR 60 - Subpart OOO provided that the permittee shall comply with any more stringent requirements as may be forth under **SPECIFIC REQUIREMENTS**, Section (A) of this permit.

3. As for any testing required by this permit or the Director, the permittee shall submit to the Director of the Division of Air Quality a test protocol detailing the proposed test methods, the date, and the time the proposed testing is to take place, as well as identifying the sampling locations and other relevant information. The test protocol must be received by the Division no less than thirty (30) days prior to the date the testing is to take place. Test results shall be submitted to the Division no more than sixty (60) days after the date the testing takes place.

4. Monitoring, Record keeping and Reporting sufficient to demonstrate compliance with the specific emissions limits and operating parameters set forth in Section A, Specific Requirements, of this permit shall be maintained on-site for at least five (5) years and shall be made available to the Director or his/her duly authorized representative upon request. All requested records must be signed by a "Responsible Official" within 10 days of the request using the CERTIFICATION OF DATA ACCURACY statement (See Attachment A) which is to be attached to, or copied to the reverse side of each reporting form.

5. In complying with all applicable federal regulations, all notices and reports required to be submitted to the Administrator of the United States Environmental Protection Agency ("U.S. EPA") shall be also submitted to the Director of the Division of Air Quality in accordance with the requirements of the applicable federal regulation.

6. All reports including testing protocols required under the terms and conditions of this permit shall be forwarded to:

Director
WV DEP - Division of Air Quality
7012 MacCorkle Ave., SE
Charleston, WV 25304-2943

And

WV DEP - Division of Air Quality
NCRO
2031 Pleasant Vally Rd., Suite 1
Fairmont, WV 26554

7. The pertinent sections of 45CSR14 applicable to this facility include, but are not limited to, the following:

§45-14-7.1
Any person proposing to construct, or relocate a major stationary source or major modification shall meet each applicable emissions limitation promulgated by the Director and any applicable emissions standard or standard of performance under 40 CFR 60, 61, and 63.

§45-14-7.3
Any person proposing a major modification of a stationary source shall apply best available control technology for each regulated pollutant for which such proposed major modification would cause a significant net emissions increase from such source. This requirement applies to each proposed emissions unit at which a net emissions increase in the pollutant would occur as a result of a physical change or change in the method of operation in the unit.

§45-14-18.1.
A permittee may petition the Director for a transfer of a permit previously issued in accordance with this rule. The Director shall approve such permit transfer provided the following conditions are met:

§45-14-18.1(a)
The permittee, in the petition, describes the reasons for the requested permit transfer and certifies that the subject source is in compliance with all the provisions and requirements of its permit, and

§45-14-18.1(b)
The transferee acknowledges, in writing, that it accepts and will comply with all the requirements, terms, and conditions as contained in the subject permit.

§45-14-18.2.
The Director shall suspend or revoke a permit if, after eighteen (18) months from the date of issuance the holder of the permit cannot provide the Director, at the Director's request, with written proof of a good faith effort that such construction, modification, or relocation has commenced and remains ongoing. Such proof shall be provided not later than thirty (30) days after the Director's request.

§45-14-18.3.
The Director may suspend, modify, or revoke the permit if the plans and specifications upon which the approval was based or the conditions established in the permit are not adhered to.

C. GENERAL REQUIREMENTS

1. In accordance with 45CSR30 - "Operating Permit Program", the permittee shall not operate nor cause to operate the permitted facility or other associated facilities on the same or contiguous sites comprising the plant without first filing a Certified Emissions Statement (CES) and paying the appropriate fee. Such Certified Emissions Statement (CES) shall be filed and the appropriate fee paid annually. A receipt for the appropriate fee shall be maintained on the premises for which the receipt has been issued, and shall be made immediately available for inspection by the Secretary or his/her duly authorized representative.

2. Approval of this permit does not relieve the permittee herein of the responsibility to apply for and obtain all other permits, licenses, and/or approvals from other agencies; i.e., local, state, and federal, which may have jurisdiction over the construction and/or operation of the source(s) and/or facility herein permitted.

3. The permitted facility shall be constructed and operated in accordance with information filed in Permit Application R14-0024 and any amendments thereto. The Secretary may suspend or revoke a permit if the plans and specifications upon which the approval was based are not adhered to.

4. At such reasonable time(s) as the Secretary may designate, the permittee shall conduct or have conducted test(s) to determine compliance with the emission limitations established in the permit application and/or applicable regulations. Test(s) shall be conducted in such a manner as the Secretary may specify or approve and shall be filed in a manner acceptable to the Secretary. The Secretary, or his/her duly authorized representative, may at his option witness or conduct such test. Should the Secretary exercise his option to conduct such test(s), the permittee shall provide all the necessary sampling connections and sampling ports to be located in such manner as the Secretary may require, power for test equipment, and the required safety equipment such as scaffolding, railings, and ladders to comply with generally accepted good safety practices. For any tests to be conducted by the permittee, a test protocol shall be submitted to the DAQ by the permittee at least thirty (30) days prior to the test and shall be approved by the Secretary. The Secretary shall be notified at least fifteen (15) days in advance of the actual dates and times during which the test will be conducted.

5. In the event the permittee should deem it necessary to suspend, for a period in excess of sixty (60) consecutive calendar days, the operations, either in whole or in part, authorized by this permit, the permittee shall notify the Secretary, in writing, within two (2) calendar weeks of the passing of the sixtieth (60) day of the suspension period.

6. The provisions of this permit are severable and should any provision(s) be declared by a court of competent jurisdiction to be invalid or unenforceable, all other provisions shall remain in full force and effect.

7. The permittee shall notify the Secretary, in writing, within fifteen (15) calendar days of the commencement of the construction, modification, or relocation activities authorized under this permit.

8. The permittee shall notify the Secretary, in writing, at least fifteen (15) calendar days prior to actual startup of the operations authorized under this permit.

9. This permit is transferable in accordance with the requirements outlined in Section 10.1 of 45CSR13.

10. Violations of any of the conditions contained in this permit, or incorporated herein by reference, may subject the permittee to civil and/or criminal penalties for each violation and further action or remedies as provided by West Virginia Code 22-5-6 and 22-5-7.

11. At such time(s) as the Secretary may designate, the permittee herein shall prepare and submit an emission inventory for the previous calendar year, addressing the emissions from the facility and/or process(es) authorized herein, in accordance with the emission inventory submittal requirements of the Division of Air Quality. After the initial submittal, the Secretary may, based upon the type and quantity of the pollutants emitted, establish a submittal frequency other than on an annual basis.

ISSUED BY: _____

JOHN A. BENEDICT, DIRECTOR
WV DEPARTMENT OF ENVIRONMENTAL PROTECTION
DIVISION OF AIR QUALITY

DATE SIGNED: March 2, 2004

ATTACHMENT A

CERTIFICATION OF DATA ACCURACY

CERTIFICATION OF DATA ACCURACY

I, the undersigned, hereby certify that all information contained in the attached _____, representing the period beginning _____ and ending _____, and any supporting documents appended hereto, is true, accurate, and complete based on information and belief after reasonable inquiry.

Name (Type or Print): _____

Signature[1]: _____

Title: _____

Date: _____

Telephone No.: _____

Fax No.: _____

[1] This form shall be signed by a "Responsible Official". "Responsible Official" means one of the following:

a. For a corporation: the president, secretary, treasurer, or vice-president of the corporation in charge of a principal business function, or any other person who performs similar policy or decision-making functions for the corporation, or a duly authorized representative of such person if the representative is responsible for the overall operation of one or more manufacturing, production, or operating facilities applying for or subject to a permit and either (i) the facilities employ more than 250 persons or have a gross annual sales or expenditures exceeding $25 million (in second quarter 1980 dollars), or (ii) the delegation of authority to such representative is approved in advance by the Director;

b. For a partnership or sole proprietorship: a general partner or the proprietor, respectively;

c. For a municipality, State, Federal, or other public entity: either a principal executive officer or ranking elected official. For the purposes of this part, a principal executive officer of a Federal agency includes the chief executive officer having responsibility for the overall operations of a principal geographic unit of the agency (e.g., a Regional Administrator of U.S. EPA); or

d. The designated representative delegated with such authority and approved in advance by the Director.

COMMONWEALTH OF VIRGINIA
DEPARTMENT OF ENVIRONMENTAL QUALITY
SOUTHWEST REGIONAL OFFICE

****

PUBLIC HEARING BEFORE THE
STATE AIR POLLUTION CONTROL BOARD

****

JUNE 25, 2008
9:15 a.m. -- 6:15 p.m.
RICHARD LANGFORD, CHAIRMAN
STATE AIR POLLUTION CONTROL BOARD

REPORTED BY: Caroline Lane, Court Reporter

APPEARANCES

STATE AIR POLLUTION CONTROL BOARD MEMBERS

RICHARD D. LANGFORD, CHAIRMAN
HULLIHEN W. MOORE
VIVIAN E. THOMSON
BRUCE C. BUCKHEIT
JOHN N. HANSON
(Telephonically Present, at 2:30 p.m.)

APPEARANCES, DEQ

DAVID K. PAYLOR
ROB FEAGINS
CINDY M. BERNDT
MIKE KISS
MIKE GREGORY
MARGARET KEY
TAMERA THOMPSON
DORIS McCLEOD

APPEARANCES, DOMINION

EVA T. HARDY
PAMELA FAGGERT
MARK MITCHELL

ALSO PRESENT: CARL JOSEPHSON, OFFICE OF THE ATTORNEY GENERAL, COMMONWEALTH OF VIRGINIA

I N D E X

PROCEEDINGS

MR. LANGFORD: Good morning. Thank you for being here and thank you for your indulgence while we get everything set up this morning.

This is a meeting of the State Air Pollution Control Board.

We will be working on the Dominion Virginia City Power Plant permit today, a continuation of the meeting we had yesterday.

I would like to ask my fellow board members to introduce themselves again for those who may not have been here yesterday.

And I will start to my left.

MR. MOORE: My name is Hullihen Moore. I am from Richmond, Virginia.

MS. THOMSON: Vivian Thomson, Charlottesville, Virginia.

MR. LANGFORD: My name is Richard Langford. I am the chairman of the board and I'm from Blacksburg.

Is this really on?

(Whereupon there was a discussion held off the record.)

MR. BUCKHEIT: Bruce Buckheit from

Fairfax, Virginia.

MR. PAYLOR: David Paylor, DEQ Director.

MR. JOSEPHSON: Carl Josephson, the Office of the Attorney General.

MS. THOMSON: While Richard is back looking for an attendant, I just wanted to express my thanks and the thanks of the board for the many thoughtful comments that we heard yesterday, and that we have received over the past many months.

Of course, you have gathered that we have been working hard for these many months, incorporating all kinds of information, working with DEQ to give our best thought to this process.

But yesterday will certainly stand out in my mind for the many different faces and really thoughtful remarks that were brought to our proceedings.

You really do matter. Those of you for whom it took courage -- had to muster courage to come to the microphone, I thank you for doing that because your voices really do matter. We really are listening. It is really our privilege to listen to what you have to say

and then to give our best efforts to these deliberations.

I bicycled these past two days up to Flagrock Recreation Area from Norton, and I saw the sun rise on both mornings and was struck by what you-all know you have, which is extraordinary natural beauty. So it has also been a privilege on my part to become familiar with a part of the state I hadn't known much about before -- both the natural beauty and the people as well.

So thank you for inviting us in your midst. Thank you for having us.

One final comment -- I noticed on the way to Wise this morning that George C. Scott was born here.

And from the comments that I heard yesterday, I know that your community is full of wonderful thoughtful people, and one of those made her way to the University of Virginia where she was one of my best students ever. And I guess I just want to say her name here and thank you for sending Kalil Whitten to the University of Virginia from Wise.

MR. BUCKHEIT: Richard had to step out

for a minute.

MS. THOMSON: Well, I guess we would like to begin the agenda, and I guess we first have the Department of Environmental Quality presentation.

MR. FEAGINS: Good morning, Chairman Langford, and members of the board, Director Paylor, Mr. Josephson.

My name is Rob Feagins, and I am the air permit manager in the Southwest Regional Office for DEQ over in Abingdon, which is not too far from here.

And I will echo many of the statements that were made yesterday. Welcome to Southwest Virginia, board members.

Our office was responsible for receiving and processing the permit application for the prevention of significant deterioration permit for the Dominion Virginia City hybrid energy center project.

And the staff that was responsible for doing the engineering evaluation and drafting the permit and helping us in a lot of support activities related to that multi-year project is here today to support us and hopefully

answer questions.

I am going to go as quickly as I can through the first few slides, because I'm sure you're familiar with many of the aspects of a PSD permit review, but at the top of the list, as with anything the government does, there is considerable adminstrative processing required.

Notification letters have to go out on time, different reviews have to be done by certain dates and things like that, and I won't get into that.

And then there is the technical review. And that is what our engineering staff is involved with.

We do the BACT analysis, the air quantity analysis, the additional impact studies that are done through the PSD permit application and the Class One impact analysis.

And then finally we wrap up with public participation, which is where we have recently come to the end of that process in which we are required by your rules to conduct a briefing, a hearing, and have a public comment period.

And as you have alluded to already, we have done a considerable amount of that, and we

have had multiple hearing nights. We have had 60 days of public comment to receive public comments on the PSD application, and of course we had the briefing.

Dominion has done their part of the public participation that is required by the rule, namely their briefing. That was done in October 2006.

So we believe we have completed these main phases of the PSD review process.

To expand just a little bit on the BACT analysis, and the way we approached that, in the application, Dominion indicated that they were applying for a circulating fluidized bed coal waste and biomass combuster.

And we looked at that technology and the control technologies that they proposed to use with that electrical generating technology, and we agreed with the application that the control technologies proposed, and that is the flue gas and sulfurization and baghouse control would be the best available control technology for the process.

So from there, we moved on to establish what appropriate emission limits would be.

And we do that by examining a number of sources, and I'll get to the slide a little bit later, that shows a few of the sources that we looked at.

I would like to say here, that we did not ignore fuel cleaning entirely, although it was not part of the cost analysis of the BACT application. It was not fully ignored. We looked at the technology that was proposed. We looked at the type of fuels that are available to them in Southwest Virginia, and we believe that for this project, that the fuels available in Southwest Virginia, the fuels they proposed to use, would be acceptable in this technology.

Now, this is a short list of many of the sources that we examined for comparable and emission limits.

And members of the board, you have sheets available to you -- we provided those -- on the sulfur dioxide and particulate matters which lists fairly exhaustively the sources we looked at and gives some technical data for that.

And as you can see, we did not ignore any of the sources listed there -- the AES Puerto Rico I know has been a source of concern with

many individuals, and we did look at it.

And we considered the Deseret facility. It is important to note that that facility has not been constructed and is not in operation.

So in the BACT analysis, we are somewhat limited to the amount of consideration we can give limits and permits that are issued but for the facilities that are not constructed and compliance with those limits is not demonstrated.

The next slide is a graphical representation that we put together just for the S02, the sulfur dioxide permit limit comparison. But it is not exactly on an even playing field here, because many of the permits have different averaging periods for their sulfur dioxide emission limits.

As you can see, the default for the table is a 24-hour limit except for, we have specified in the margin, that some of them have three-hour limits and some of them have 30 days. It just bounces all over the place.

But there are -- if you look at the dark green bar in the middle -- that's the Virginia City hybrid energy center project. And that is

the sulfur dioxide emission limit on a 30-day average that we are proposing in the revised draft permit, that came out of our Response to Comments document, which I am sure you have seen.

And you can see that there are three other facilities depicted in the graph that have what appear to be lower emission limits.

The one on the far left, the light green is the AES Puerto Rico facility.

And the two on the far right are the Highwood and the Deseret, which are not demonstrated limits.

So those were not part of the final consideration for the BACT limit for the Virginia City hybrid energy center.

As I said earlier, we did consider the AES Puerto Rico facility.

Its type of fuel is starkly different than what we find in Southwest Virginia.

They have -- of course they import their coal. They are an island or an island territory, and it comes, we understand, from Columbia. And it has a range of sulfur somewhere .4 to .6 weight percent, which is

extraordinarily low, and it is something we don't see in Southwest Virginia, even in clean coal.

And there are some other issues with the AES Puerto Rico limits.

If you dive down into the details a little further, you will find that their particulate matter limit is a little over twice our proposed particulate matter limit.

And we have -- our engineers have speculated that the reason for this could possibly be that they are loading the system with limestone for the flue gas desulfurization in order to meet what appears to be a sulfur dioxide limit that is a little bit out of line with everything else in the nation.

Now, just to touch on some of the other limits that we established in the permit, we have found in our research at the time we did the engineering analysis and since, during your information gathering efforts, that we have among the best limits for -- especially N0x and PM in the nation for this type of technology, for the circulating fluidized bed technology.

I don't believe, if you go out and do a

search, you will find a better N0x limit than what we proposed.

The total PM10 limit, which is condensable and filterable, the three-hour limit that you see there -- 0.012, likewise is among the best in the nation.

It is true you may be able to find a number slightly different than that in another permit, but you would be able to perhaps disqualify that number in the BACT analysis or based on the fuel properties, the way they operate the system, et cetera.

And then it is important to note here that in Virginia we have the only permit that we could find where we have proposed the PM2.5 limit to go into the PSD permit.

And as we discussed earlier, these are a couple of other different aspects of the PSD permit review -- the modeling analysis was approved by our air quality modeling section and conducted by the applicant.

And it shows very clearly, that the impact from this facility is in compliance with the National Ambient Air Quality Standards and the PSD increments.

And that is in contrast to many of the comments that we have received. But it is clear that there are no increment violations, and no MACT violations, that this source is a contributor to.

And then the additional impact analyses that are required by the PSD rules were done, and the results of all that is favorable.

Now on the next slide -- I would like to stress these two points in response to some of the comments that were heard yesterday and that have been seen in the submittals -- the Class One impact analysis -- the federal land managers -- the national, the Park Service and the Forest Service, neither of the federal land managers with those jurisdictions, had a finding of adverse impact.

And it has been -- at least what I heard yesterday, it was stated over and over that perhaps there was an adverse impact in one of these Class One areas.

Indeed there was not. They did not find any adverse impact in that area that they notified us of.

And furthermore, during the public

comment period, the EPA provided no comments on the permit.

And you can read into that what you will, but generally when they do that they are satisfied with the mitigation plan that we put in place after we negotiated with the federal land manager and they are satisfied with the BACT analysis.

So we will move on to the public participation process, and I will just show you here the highlights of what we found in the public comment and our analysis of the comments. And the next two slide has those major categories that we pulled out, and that we addressed in our Response to Comments document, which I believe you had an opportunity to review, which were released by DEQ the week before last.

And I won't read these, but you can see that there are a number of important categories there, and we feel like we have adequately addressed those in the Response to Comments document.

Now, as part of the department's response -- reviewing these comments, Response to

Comments, we have proposed as you again can see in the Response to Comments document and in the draft permit that we provided you as a result of that, some changes that we are going to recommend.

The top of the list there, we have modified the draft permit to show that we're going to require a particulate monitor for measuring filterable particulate. The technology we believe exists to measure that and one of the board members -- I believe it was Mr. Buckheit, earlier in the process asked us to consider that, and we did, and we worked with the source, and that condition is now there for them to put a CEMS for a filterable particulate matter.

The next bullet down -- because of that -- partly because of that and partly because of our review of another permit, namely the Spurlock Number 4 permit, which is Eastern Kentucky Power Cooperative, we believe that a limit of 0.009 pounds per million BTUs for filterable particulate matter is fitting.

And since it can now be measured with CEMS, it all comes together and makes sense.

And the next two bullets -- and these aren't in any particular order -- but the next two bullets are just a couple of housekeeping issues.

The first of the next two bullets is a little bit more important than the second one, and you will hear a little bit more about that later, I am sure in the Department's presentation on the Article 7 permit -- but when we originally developed the PSD permit, as you are aware, the new source performance standard subpart (D)(a) was in place and so was the Clean Air and Mercury Rule, and part of NSPS Subpart (D)(a) was a requirement to have a limitation for mercury.

They in essence named mercury as a Clean Air Act Pollutant in Section 111 of the Clean Air Act.

And by doing so, we believe that it was a regulated pollutant under PSD, and should be considered for BACT and we did put BACT limits on mercury in the PSD permit.

But when that rule was changed, mercury went away in the Da so strictly speaking it is no longer subject to BACT under PSD. It is no

longer subject to regulation under Da, but it will -- as you will hear later in the department's presentation on the MACT permit, come under regulation there.

So what we did, we went through and carefully -- hopefully -- carefully enough -- removed the regulatory citations from all the conditions where we had the limits for mercury.

We did not change the limits for mercury. We retained the limits in there. We did not want to relax any limits, and we thought taking the limit away would be a relaxation. We did not want to do that. So we left the limit we had in there before, and we used general authority from the regulations as citation for retaining the limit.

So there remains a mercury limit in the PSD permit. It is just not a BACT limit and it is not there as a result of NSPS Da.

The next item NSPS -- we call it "Quad I" -- IIII, is for the types of internal combustion engines.

And the department does not have a delegation of authority for this particular rule at this time. So those citations,

justifiably so, should be removed.

Again, the permit conditions for these units remain unchanged, as they did in the draft. It's just that the regulatory citations have been removed.

The bottom item on this page is quite an important item, and it is one that discussions with the source and with individual members of the board led to us believe that a reduction in the sulfur content limit of the fuel would be appropriate.

And we have put a limit in the permit in addition to the previous one -- if you recall, it's 2.28 percent on an as-fired basis. We have added an additional limit there of 1.5 weight percent on an annual basis.

So over a year's time, the fuel sulfur content would average no more than 1.5 weight percent.

The next slide -- the facility does have a continuous emission monitoring system, or CEMS for sulfur dioxide, and with the lower sulfur content limit, if you will, and after reviewing, specifically, the Deseret permit, we believe that it would be appropriate to put in

a 0.09 pounds per million BTU limit for sulfur dioxide, where one did not exist before.

We had other shorter term limits -- if you recall the .12 pound per million BTU limit was in the original draft permit on a shorter term basis, but we believe that it is appropriate now to adopt this limit.

And if one back calculates, if you will, to see what a comparative control efficiency is for certain types of fuel under certain conditions, it works out to be well in excess of 98 percent.

And commensurate with that, there should be a change in the annual sulfur dioxide emissions, which is the next bullet -- and just doing the arthmetic -- and it is illustrated in the Response to Comments document for you, the new annual sulfur dioxide limit becomes the 2,469 tons.

And because the facility's sulfur dioxide limit, annual sulfur dioxide limit was closely tied to the federal land manager's mitigation plan, which is also included in the draft PSD permit, we believe that it was appropriate to halve -- cut in half, that resultant limit of

2,469 and just roll that down into the federal land manager's mitigation plan so they have to mitigate down to 1273 tons.

Before it was half of the previous number, so we just adopted the same proportion here, and cut that number in half.

MR. LANGFORD: Rob?

MR. FEAGINS: Yes, sir.

MR. LANGFORD: Are there copies of your presentation available?

The one we were handed doesn't have any of your slides on it.

MR. FEAGINS: Okay.

MR. LANGFORD: I don't know if they are available or not.

MR. FEAGINS: They are available. I gave them to Cindy this morning. I will look in just a moment.

I have one additional copy and I'll ask Mike Gregory to bring it up. I apologize for that.

MR. DOWD: I think Cindy may have --

MR. LANGFORD: I have a presentation, but it isn't yours.

Do we have them somewhere?

MR. FEAGINS: Would you like for me to proceed?

MR. LANGFORD: Yes.

MR. FEAGINS: Okay. The next slide is a continuation of the changes we have proposed to the PSD permit. And logically so, if the sulfur dioxide emission limitation is being changed or reduced, then the sulfuric acid in this limitation, we believe should likewise be changed, and you can see here we proposed a new lower short-term limit, and the resultant long term limit, the annual limit has been lowered as well.

This next bullet about the removal of mercury BACT regulatory citations goes back to what I said before.

It gets a little more involved than just taking the citations out. At some point we actually had to go in and revise the wording of some of the conditions to specify how we wanted the facility to keep records and monitor mercury and so forth, because previously we had simply referenced the NSPS subpart.

So it became a little more complex. We had to go in and spell out the exact method for

doing that. And that is what I am trying to represent by that bullet.

And then the last one is just simply a housekeeping note that we added one or two words to a condition to clarify that we expected from the source the submittal of a monitoring protocol and that's for the PM2.5 monitor that we specified in the permit.

And then the final slide is simply a statement of the staff's recommendation that the board consider and approve the draft permit as we have proposed, with revisions.

Now, there have been a couple of additional revisions, and again Cindy was given a sheet of these changes. And I hope that they made their way to you. If not, we will do our best to locate those.

But subsequent to giving you the draft permit that came from our Response to Comments document, we have found that the particulate matter limit, the annual particulate matter limit should be reduced by an amount commensurate with the reduction that is realized from the document 30-day limit.

And she has been given -- she details

that change.

And then the last two items on the sheet that Cindy was to have given you --

MS. BERNDT: I did.

MR. LANGFORD: I don't think we --

MS. BERNDT: It's there.

MR. LANGFORD: I think we got it back. And even the one you gave me -- the one we have up here is not your presentation. It's the next presentation. It's the MACT prsentation.

Cindy, do we have copies of the PSD presentation?

MS. BERNDT: I am looking.

Oh, I thought they were the same thing. I apologize.

MR. LANGFORD: And I am supposed to have a -- that was handed out this morning.

MS. THOMSON: I have a couple of questions for you, Rob.

You indicated that there was no finding of adverse impact by the either of the federal land managers.

The finding of adverse impact is -- the Clean Air Act -- if there is a finding of an adverse impact on a Class One area by a federal

land manager and the department and the board agree with that finding of adverse impact, we must deny the permit.

Is that not the case?

MR. FEAGINS: Or find methods to mitigate or resolve the issue.

I believe you are correct.

MS. THOMSON: That is a pretty big hammer.

So if we say there was no finding of adverse impact, still the National Park Service and the USDA Forest Service raised some fairly strong concerns about the proposed emissions from this facility.

Is that not correct?

MR. FEAGINS: That is correct. There was some concerns raised by Bill Jackson of the Forest Service and Mary Sue Hilliard.

And as a result of that, the mitigation plan came forth to resolve some of the issues related to sulfur deposition and visibility impacts that they thought would happen within their areas of concern.

MS. THOMSON: Right. And there was that agreement reached, but I just want to -- for

the record -- read some of the conclusions that were included in part of the Forest Service's comments and basically what they said is that that deposition has to -- sulfur deposition in Linville Gorge has to drop to a very low level in order for acidification to be reversed and for streams to be restored in that area.

The Forest Service basically was saying, as I understand it, that the mitigation is good, and that they certainly did not make a finding of adverse impact, but still everything I read in the comments indicates that the Forest Service is still very concerned about additional sulfur deposition in their protected area because in the Southern Appalachian, sulfur has banked to such a great extent in soils of ecosystems that it is going to take a very very long time and very great reduction in sulfur depositions for that sulfur to be flushed out and for biological and chemical recovery to begin.

So I just wanted to add that important qualification to the fact that, yes, the Forest Service and the Park Service did not actually make a finding of adverse impact, but they

still registered a very strong concern about additional sulfur emissions in the area.

And we also received some comments from the National Park Service in the formal comment period, and last week when they discovered that they had not been informed of the April 15th to May 15th posting of board comments.

And I wonder if you could summarize the National Park Service comments from last week?

MR. FEAGINS: I will address the comments that relate to what I believe are the PSD issues. And I believe our air quality modeling section could address the air quality aspects of Mr. Shepherd's statements.

As you have stated, the National Park Service did not have a formal finding of adverse impact, and Mr. Shepherd continues to supply his input on the project.

The first item that I picked out of his statement to be addressed, he says: The Virginia City hybrid energy center would be capable of mixing assorted fuels to produce a consistent blend compatible with IGCC.

And this goes back to a lot of our statements in our Response to Comments document

about the appropriateness of IGCC and alternative technologies and so forth.

But his statement on the surface may be true. Certainly, they could blend fuels to a consistent level, and that could be done.

But my understanding -- my engineering understanding of IGCC, as limited as it may be -- is that these facilities have to have a constant diet of a more or less uniform type of fuel.

And if we get into reading what Mr. Shepherd has proposed here that, yes, it can handle anything in Southwest Virginia, seemingly in any proportion -- I do not believe that to be true.

I believe, yes, it could be designed to handle Southwest Virginia fuels in a constant diet -- a constant stream or composition -- but not necessarily in an available manner as the Virginia City hybrid energy center hopes to take advantage of our available fuels -- fuels of opportunity, and so forth and mix them in different proportions at different times.

So that's the response to the first one.

And then the second one I identified --

it says: CFB technology is relatively dirty compared to modern pulverized coal technology, which is now being proposed to be permitted at lower limits for S02 and NOx, because the primary justification for use of C02 technology is the ability to burn gob. The minimum gob burning requirement should be included in the permit to justify higher emission limits.

Well, again Mr. Shepherd has continued to dwell on comparing our limits in our draft PSD permit, which is subject to BACT review, to limits that are not demonstrated, and in some cases, permits that have not even been issued.

He has done that over and over.

But again, my statement which goes back to what I made in my presentation is that the SO2 limits that we have in the revised draft permit are very very much in line with what they should be when one considers the type of fuels and fuel blends that we are burning for this type of technology having the air pollution control technology that it would have.

And again it goes back to the desire to allow them to have fuel flexibility to burn the

fuels of opportunity in Southwest Virginia.

The next statement from the National Park Service -- and I apologize -- these statements are lengthy -- I am reading this, trying to summarize it.

While EPA guidance does not require that a permitting authority evaluate alternative combustion technologies, neither does it prohibit it.

For example, New Mexico and Illinois have required evaluation of IGCC as part of their BACT determination process. DEQ does not need federal permission to require consideration of IGCC in its BACT analysis.

It is the prerogative of DEQ to determine what emission limits best serve the Commonwealth, and represent BACT and leave it to the applicant to meet those limits -- if that means redefining the source.

The applicant did provide evaluation of IGCC and the department considered it as part of our engineering analysis. And in our Response to Comments document, we evaluated IGCC, not as a BACT alternative technology, but as in the interests of being exhaustive and

thorough, we did look at it.

We believe we -- again we have established limits in the permit that are representative of BACT, and in several cases the permits are as stringent as what we see in IGCC installations that are in operation.

And then our Response to Comments document addresses the topic of IGCC as BACT, and we believe that that would be a redefinition of the type of source that the company has applied for.

The next statement that I identify in this write-up says: DEQ should consult with Tampa Electric to obtain its advice on the reliability and economics of IGCC.

Well, my experience with -- I guess it is Tampa Electric Power Company in Florida is that they have only recently gotten to where the operation is somewhat reliable.

But in any regard, in comparison of the costs of operating the Tampa Electric Facility with the Virginia City hybrid energy center would be an apples-to-oranges comparison, in our opinion, because we are not considering IGCC as a BACT alternative.

The next statement from Mr. Shepherd: Despite DEQ's apparent emphasis upon demonstrated emission limits, none of the limits cited above by DEQ have been demonstrated.

The draft permit for East Kentucky Power, units one and two, would limit NOx to .07 pounds per million BTU on a 24-hour average basis.

We assume that when the permitting authority issues or proposes to issue a permit, it has a realistic belief that the limits contained in those permits can be achieved.

Now, the commenter's last statement there, "realistic belief" is the key to our standing on this position.

We are not required to look for the lowest number when establishing BACT.

We look for limits for similar demonstrated technology.

And we look for limits that are realistic from the standpoint of being enforceable as a practical matter, within the confines of the control technology and the BACT limits.

So in that regard, his statement gives us

the latitude of looking at limits that we believe can be met within the confines of BACT.

MS. THOMSON: If I could break in here just one minute.

I appreciate your detailed response to my question.

I guess sort of backing up to where I started from, which is the issue of sulfur deposition, and concerns raised on that score, we have already gone over the USDA Forest Service comments, and last week in the National Park Service's letter, they said: Our primary concerns relate to the proposed 24-hour emission rate for sulfur dioxide.

Modeling conducted by the applicant indicates that its proposed 24-hour S02 emissions would significantly impact both S02 increment and visibility at Great Smoky Mountains National Park, a Class One area administered by the National Park Service, and continue to believe that there are technological solutions to those problems.

S02 emissions can be reduced by changing the basic premise of the project from the CFB to IGCC, or by making more effective use of the

proposed S02 control technologies.

So that was -- the two sets of comments I think are closely linked.

And again while my point here is that while of course neither federal land manager made a formal finding of adverse impact, which is a very large and serious hammer, they continue to register their strong concerns about additional sulfur depositions in the area.

MR. BUCKHEIT: If I may?

MR. LANGFORD: Let me make one comment, then I will allow you, Bruce.

The letter that's referred to here from Mr. Shepherd was -- as was mentioned, was received after the public comment period was closed.

In addition, many of the comments that he makes are actually comments about staff's Response to Comments that were received during the official public comment period.

While the information he provided could be of interest to us, I just want to make sure the record reflected that it was not the kind of comments that would have normally been

presented, even if he had been aware of the regular comment period, because he wouldn't have had access to Response to Comments.

I just want to get that on the record.

Bruce?

MR. BUCKHEIT: Yeah, Rob.

First of all, thank you and the DEQ staff for all the work you guys put in for the last few years, for the weekends and evenings that went into this.

But with respect to these letters that Dr. Thomson has been talking about -- are they right?

MR. FEAGINS: In --

MR. BUCKHEIT: In saying that it would significantly impact whatever they just said about --

MS. THOMSON: Increments.

MR. BUCKHEIT: Increment consumption I guess.

MS. THOMSON: Yes. And visibility at Great Smoky Mountains National Park.

MR. KISS: Good morning, members of the board.

My name is Mike Kiss. I am the modeling

coordinator in Richmond.

And I guess I would break Mr. Shepherd's comments down into two parts.

One is Class One increment -- and really, there is no such thing as "significance," in terms of increment if there is not an increment violation.

There is available PSD increment that a source can consume, and it is allocated on a first-come-first-serve basis.

So the comments are a bit confusing in terms of the terminology.

MR. BUCKHEIT: So is it consuming the increment?

MR. KISS: Yes.

MR. BUCKHEIT: It is legal to do so, but it is consuming the increment.

MR. KISS: It is consuming a portion of the increment that it is allowed to do.

MR. BUCKHEIT: What portion of the increment?

MR. KISS: It depends on -- it is a small amount -- a very small fraction, and there is different increments for different averaging periods.

MR. BUCKHEIT: Right. Well, any new construction would consume some fraction.

I am trying to figure out whether this is important or not.

MR. KISS: No. It is up to the state to track increment consumption, and so we do that on a continuous basis. And we make sure that as sources come online, we are not exceeding that increment.

MR. BUCKHEIT: And I guess I want to press one more time for: How much of the increment?

Because if we're overly lax in the permitting process for S02 emissions for this facility, it would mean that other facilities can't come into the area because they might bump up against the increment.

MR. KISS: I could give you the total amount -- the total amount of increment consumption, and it depends on the pollutant, obviously.

MR. BUCKHEIT: Let's talk about S02.

MR. KISS: It's going to take me a minute to find the number.

MR. BUCKHEIT: That's okay.

MR. KISS: Thank you.

The PSD increment consumption -- we have a total value here, not the individual source's contribution -- on a 24-hour basis, 4.58 is the increment consumption with a Class One increment being a value of five, and on a three-hour basis, the total increment consumption of all sources is 14 micrograms per cubic meter and the increment is 25.

So we are getting close to --

MR. BUCKHEIT: The first one is 4.58 out of 5?

MR. KISS: Out of 5. That is the total impact of all sources that consume increment.

We don't have it broken down at this point.

MR. BUCKHEIT: Well, is this source consuming like half of that?

MR. KISS: No. It is a very small fraction. I don't know the exact percentage offhand at this point.

MR. LANGFORD: Can you give us an idea of -- you don't know the exact percentage?

Is it 5? 50? 80?

I mean, you said small.

MR. KISS: It's probably in the order of the less than 10 percent of the value.

The other part of Mr. Shepherd's comment was with respect to visibility.

And again the threshold for adverse impact is defined under Section 165 of the Clean Air Act.

There really is no such terminology in terms of significance. It is either an adverse impact or it is not with respect to the air quality related value.

Now, in terms of the visibility impact, the National Park Service and the federal land manager as a whole use different thresholds for visibility impairment.

And those thresholds were looked at and there are a handful of days where the source may impact visibility in Great Smoky -- and we are talking about roughly seven days over the course of a year.

And keep in mind, when this particular source would affect visibility in the Great Smoky Mountains, the wind would have to be out of the north or the northeast.

Now we know that during those times --

most of time, the air quality is going to be relatively good.

So even though the source may be contributing to visibility impairment, the wind directions that are associated with that impairment lead to generally good air quality.

MR. BUCKHEIT: And where are we with the PM2.5.

MR. KISS: The source did do a PM2.5 air quality analysis. And it demonstrated compliance with the standards.

MR. BUCKHEIT: What about increments?

MR. KISS: There is no PM2.5 increment, but they are in compliance with the PM10 increment.

MS. THOMSON: Your comments indicate that there is no formal regulatory that comes into play when you have got an increment consumption of 4.58 in a 24-hour, and the increment is -- allowable increment is 5.0.

Similarly, you indicated that if there is no finding of adverse impact on an AQRV, there is no regulatory determination.

However, that doesn't change the physical fact, which I think both the Park Service and

the Forest Service are pointing to, which is that sulfur loading in this area have been historically very high, that the sulfur dioxide increment consumption is relatively high overall, not just from the source, but overall.

And that again, going back to the Forest Service's comments, which rest on a very large body of scientific information, that sulfur deposition has been, as we know, in the Southeast and Northeast are very high, and that in the south, unlike parts of the Northeast, sulfur doesn't appear to being flushing out of the soils as quickly as in other parts of the country and streams are remaining acidified. Ecosystem recovery is estimated to take a long time.

So, yes, I take your point that there are no regulatory thresholds that have been triggered here, but I think their point goes further than that, which is pointing to the overall historical high level of sulfur loading and the long time and much reduced sulfur deposition that it is going to take for ecosystems to really come back and visibility as well.

MR. KISS: Yes. We did receive the Forest Service's comments relative to those issues.

We didn't evaluate them, because at the end of the day, the Forest Service accepted the mitigation plan, and it said it addressed their concerns.

We normally -- when there is an adverse impact in air quality related values, such as acid deposition -- those types of studies are published in the Federal Register, supporting documentation provided. And there is an opportunity for public comment.

But the staff however did not go into depth on the validity of the comments of the Forest Service.

MS. THOMSON: In order to find a recent statement about the fact that southern Appalachian streams and ecosystems are not recovering -- and you don't have to go farther than EPA's online listed 2006 progress report for acid deposition -- I could point you to the pages there. Of course, this is EPA's regular progress reports, which I know you're aware of, because I think in your comments somewhere,

there is reference to a 2003 progress report.

Since then, there have been annual reports.

In the 2006 progress report, there is a very clear statement perhaps on about page 34 or 35, to the extent that while, yes, sulfur deposition is going down, and yes, we see some recovery in the Northeast, we are not seeing it in the south.

So I would point you to that report.

MR. KISS: Yes. I am aware of that source.

MR. BUCKHEIT: Mike, I don't know if this is a question for modeling. This is for anyone in the department.

I can't believe the department doesn't have a view as to whether the studies of the adverse impacts of the Southern Appalachians -- ongoing effects of that -- are not as reported or that the department hasn't looked at it.

It may not be your responsibility, Mike, but Rob, could you speak to that?

I mean, does DEQ agree with the published science respecting the state of the Southern Appalachians?

MR. FEAGINS: There may be on some policy level which is being reviewed at DEQ. It certainly isn't on my level.

If some of the individuals from the policy department here with DEQ want to address that, I would certainly invite them to do that.

MR. BUCKHEIT: David?

MR. PAYLOR: I am -- clearly there have been problems resulting with acid rain, and much of what we have done -- it has historically been our Department of Game and Inland Fisheries looks at that and we coordinate with them in regards to recovery and mitigation and things like that.

In the Commonwealth, we have seen -- because of Title IV, the significant reductions in S02. We have seen some recovery. We still have some problems in Virginia. And I can't say that we have studied in depth the states south of us in that regard.

I have to say, as regards this particular issue, we have put a lot of emphasis on the fact that the Forest Service has found -- had a finding of no adverse impact.

They are very protective of their

properties, and when they believe there is an adverse impact, it is our experience that they say so, and we work very diligently to fix that.

So we have put considerable weight on that particular finding.

Clearly, that finding needs to be informed also by their understanding of the science, and we think that we do that.

MR. FEAGINS: Director Paylor touched on an important issue, and that is the acid rain permitting provision in the state and federal rules.

While not specific to southeast states, the implications of that are nationwide, and recognized.

MR. BUCKHEIT: And just one more sentence or two more sentences -- Dr. Thomson's point -- the published science tells us that the acid rain program has been reasonably successful in the Northeast.

But because of the differentials in buffering capacity in the south, acid rain problems showed up later. But like a larger sponge, that extra buffering capacity means

that we -- our biosphere has absorbed so much more material that it is going to take decades longer -- many decades longer, and the recommendations are that unless we significantly reduce acid deposition in our areas, we are going to have continuing problems for generations.

On their website, TVA evaluates the situation and suggests that one should simply forget about it, that progress is not possible, and the best that one can do by way of restoration is to simply help to prevent it from getting worse.

I raise all this, because it is certainly something that I have considered in thinking about the S02 levels for this particular plant. And I guess I'll stop.

MR. LANGFORD: Mr. Moore --

MS. THOMSON: Actually, I just want to read a direct quote from EPA's 2006 Acid Rain Progress Report where it talks about stream chemistry, quote: Sulfate concentrations are declining substantially in all but one of the regions.

In Southern Appalachia, however sulfate

concentrations are increasing -- and this is in the streams.

This region is unusual because its soils can store large amounts of sulfate deposited from the atmosphere. Only after large amounts of sulfate have accumulated in the soils do stream sulfate concentrations begin to increase, remain elevated until the stored sulfur is depleted.

This phenomenon is now being observed in the Southern Appalachians, despite decrease in sulfates in atmospheric deposition, end quote.

MR. FEAGINS: And we have seen much of the same information you have referred to.

We do not use that information as a mechanism to get beyond BACT in the PSD permit.

MR. BUCKHEIT: How about complying with the Virginia statute?

MR. FEAGINS: Which statute?

MR. BUCKHEIT: Virginia air law.

MR. FEAGINS: Which statute in particular?

MR. BUCKHEIT: The one that says that permits are supposed to be protective of the public health and the environment.

MR. FEAGINS: Within the confines of the PSD Rule, the permit is being processed, it is.

MR. BUCKHEIT: Virginia has its own statute, separate and apart from the federal government.

The Commonwealth did not cede all rights to the federal government when it comes to protecting Virginia's property and the health of the folks in Virginia.

MR. DOWD: Good morning. My name is --

MR. BUCKHEIT: I asked you about -- hi, Mike -- I asked you about whether under Virginia statute, one could take into consideration the adverse impacts to the environment in Virginia?

MR. DOWD: Good morning. My name is Mike Dowd, and I am the air director for DEQ.

MR. PAYLOR: Mr. Chairman, would it be proper for our counsel to answer that question?

MR. BUCKHEIT: Let me rephrase the question as to whether they did.

MR. DOWD: Mr. Buckheit --

MR. PAYLOR: Would you like to hear from counsel regarding the answer?

MR. LANGFORD: Certainly. We'll hear

from Counsel.

We will get to your answer.

MR. BUCKHEIT: Okay.

MR. LANGFORD: But Counsel has indicated a desire to address it as well.

MR. JOSEPHSON: I think the board is aware of the advice I have provided in the past on several issues, some of which relate to this particular permit application.

Virginia certainly does have its own state air pollution control laws.

But I have pointed out to the members of the board in the past, the provision -- and I can't remember the precise section -- but to the extent that the board wants to adopt regulations more stringent than federal law, it needs to notify the appropriate standing committees of the General Assembly.

To the extent that the board wants to interpret existing regulations more stringent than federal requirements, then you are aware of my advice.

If you would like for me to repeat it in a public meeting, I will.

MR. BUCKHEIT: My point is -- I am not

asking about -- I am not promulgating a regulation. I am not interpreting a regulation.

I am asking about whether the department follows Virginia law as well as federal law.

MR. JOSEPHSON: Well, I think in this case, it is kind of similar.

And the department follows its regulations adopted by the board and administrative agencies -- the department and the board are bound by their own regulations.

MR. BUCKHEIT: Right. And I don't recall any Virginia regulation that says, "Don't comply with Virginia's constitution and don't comply with Virginia's air law."

MR. JOSEPHSON: Virginia's air law was implemented by regulations. And I'm not aware of any self-executing provision in the Virginia constitution which is applicable to this permit application.

MR. BUCKHEIT: Well, under Virginia air law, is the permit not required to protect the public health and safety?

MR. JOSEPHSON: Within the constraints of the existing regulations, yes.

MR. BUCKHEIT: Did you, separate from the BACT consideration look at whether adverse environmental conditions, respecting sulfur deposition in the Southern Appalachians within Virginia cause adverse impacts and should be remedied?

MR. KISS: Typically, since the federal land managers are tasked and they understand these Class One areas much better than we do, and they understand the issues relative to those Class One areas, we did look at the deposition in the Class One areas, and we gave that information to the federal land manager.

They made the determination it did not meet an adverse impact, pursuant to Section 165.

So we feel that their scientists are better in a position to respond to their ecosystem.

MR. BUCKHEIT: But you're talking about a regulatory threshold. They commented that it was an adverse impact, in summary.

MR. KISS: Well, actually they didn't.

MR. BUCKHEIT: They didn't use the word.

MR. KISS: Normally what happens is if

there is an adverse impact, is they present their science. They say this particular facility --

MR. BUCKHEIT: Again, you have seen the federal regulatory thresholds.

I am coming back to Virginia law.

MR. KISS: This gets back to their scientists are in a better position to comment on their ecosystem.

MR. BUCKHEIT: Thank you.

MR. MOORE: Mr. Chairman.

MR. LANGFORD: Mr. Moore.

MR. MOORE: And I would just make this point -- we talked the law.

The Clean Air Act is the law, isn't it?

Mr. Josephson, would you agree with that?

MR. JOSEPHSON: The Clean Air Act is the law with respect to the federal requirements. It is the law with respect to the states to the extent that they are required to comply with provisions in the Federal Clean Air Act.

MR. MOORE: And we are operating here under the -- that we carry out the Clean Air Act.

MR. JOSEPHSON: That would be consistent

with the approved step.

MR. MOORE: But I just make that point. I would also just sort of note that I think what we're doing is the Clean Air Act, but if one wants to look at Section 1307 (e) advisory boards in approving permits shall consider facts and circumstances relevant to the reasonableness of the activity involved including scientific and economic practicalities of reducing or eliminating discharge resulting from the activity.

MS. THOMSON: Just as long as we are on definitions and law and BACT and this is, I think pulled straight from the Virginia Code: Means of emission limitation based on MACT and degree of reduction for each regulated NSR pollutant, taking into account energy, environmental, and economic impact, and other costs.

And if you look at NSR manual that term "environmental impact," is construed quite --

MR. LANGFORD: I am going to move off --

MR. MOORE: I am going to ask another.

I think I heard you -- Mike your -- this was a modeling question, I guess, that this

plant may impact visibility in the Great Smoky Montains seven days.

Did I hear that correctly?

MR. KISS: There is a contribution that exceeds a threshold that the federal land managers look at in terms of visibility impairment, yes.

As I was stating earlier, the days which this plant would impact the Class One area are generally days where we have good air quality.

So even though there is an incremental contribution, the winds are from a direction where we get good air quality.

MR. MOORE: And when -- you say that, so you may must know the time of year.

MR. KISS: Well, those wind directions can occur any time of the year. They are more frequent --

MR. MOORE: Well, then tell me -- why should I assume these seven day they are going to be blowing in the right direction, if you can't tell me: Well, it's in the summer and the wind generally blows this direction in the summer, or it is in the winter, and the wind blows from this direction?

MR. KISS: The winds from those directions, the north and the northeast, as I've talked about earlier occur more frequently in the winter, but they can occur during any season.

And the federal land managers did look at that. As part of their determination of adverse impact, they are required to look at the frequencies, the duration and the spatial expanse of the visibility impact. Based on that analysis they did not determine it to be an adverse impact.

MR. MOORE: They determined no adverse impact, but they did note -- or you determined the seven days -- was that you or was that them?

MR. KISS: It was modeling conducted by the applicant in accordance with procedures identified by the federal land managers and DEQ.

MR. MOORE: And if we did that for each power plant impacting this area, is that added on to a background amount to see that -- yes, it is important because this, in addition to everything else, would create this possible

problem every seven -- I mean, for seven days?

MR. KISS: Well, I think now you're getting into regional air quality where you're looking at multiple sources.

In the Response to Comment document, we talk about a regional haze limitation plan, and the fact that despite the increase in emissions that is being proposed from this facility, we have thousands of tons of S02 reductions regionally.

So even though this particular facility may be contributing a small fraction to visibility impairment on a select number of days, the regional air quality is going to continue to improve and we are meeting what EPA terms the "uniform rate of progress towards visibility improvement and natural conditons," by the year 2064, so -- now whether or not we get there --

MR. BUCKHEIT: I am not sure I am going to be here to see it.

MR. KISS: But we do expect to see hundreds of thousands of tons in reduction in sulfur dioxide that both acid deposition and visibility are going to continue to improve,

even with the installation of this proposed facility.

And that has been taken into account in our regional planning and modeling.

MR. MOORE: Let me just, if I may, ask this question: I assume your answer would have been the same when the limit -- was it 3200 tons?

Your answer would have been the same there and it's whatever it is -- it is that much better now?

MR. KISS: That's correct.

MR. MOORE: And it is even better because of the Forest Service -- somewhat better because of the Forest Service mitigation plan?

MR. KISS: That is correct. I think there is some other --

MR. MOORE: So each of these steps makes it a little better?

MR. KISS: That's correct.

MR. MOORE: All right. Thank you.

MR. LANGFORD: Are we ready to move on to the --

MR. BUCKHEIT: No.

MR. LANGFORD: Okay. You got some more

PSD questions?

Ten more minutes.

MR. BUCKHEIT: Always ten minutes.

Recently you-all revised your proposed permit to reduce the S02 levels from something like 3300 tons to 2400 tons.

Is that correct?

MR. FEAGINS: Yes, sir.

MR. BUCKHEIT: So that is an actual reduction?

MR. FEAGINS: Yes.

MR. BUCKHEIT: So what changed in terms of your evaluation of the engineering of the plant that would allow -- you earlier determined that 3300 was the best that could be done, and now we move to 2400 is the best that could be done.

What changed your view?

MR. FEAGINS: Well, in the Response to Comments, we evaluated a number of facilities that individuals had indicated that we should look at.

And as I mentioned before, a number of them are not constructed yet, but nevertheless we considered their emission levels.

And instrumental in establishing the S02 limit was the Deseret facility, which had a 30-day limit, which our permit does not. There is not a standard parallel with that, so we could not establish it in our permit.

But by establishing a limit comparable to the Deseret facility which is zero zero nine pounds per million BTU, doing the simple arithmetic, and extending that out for one year of operation --

MR. BUCKHEIT: I thought earlier you had rejected consideration of another facility's proposed limit because it hadn't been built yet?

MR. FEAGINS: On the basis of BACT.

MR. BUCKHEIT: So how can you accept the Deseret permit, which hasn't been built yet?

MR. GREGORY: Members of the board, my name is Mike Gregory. I am the air permitting engineer.

What we did was, we looked at the Deseret Response to Comments.

This was a document we did not have available to us the moment we were drafting our permit.

Our original S02 limit that was drafted was .12 pounds per million BTU.

We had -- that was a result of negotiations and wrangling with Dominion. They originally come in at .15 pounds per million BTUs.

And we originally felt like the 24-hour limit would be acceptable, and our annual limit was based on that.

We always knew that with a .12 24-hour limit, we would get better annual performance than the actually 32, 3300.

And when we saw Deseret's Response to Comments, we looked at several things, but one of them being the removal efficiency that they were basing their limits on, that had been a point of contention with members of the board and all along with us.

Basically, our original .12 pound per million BTU limit is in a sense based on a removal efficiency of 98.4 percent using just waste coal.

It also corresponds to a removal efficiency of 98 percent with run-of-mine coal.

And when we saw Deseret's response --

their plant burns primarily waste coal. And they were confronted with comments on AES Puerto Rico and defending their S02 limits.

They proposed setting their 30-day limit on a removal efficiency of 98.8 percent.

MR. BUCKHEIT: So it was the company that proposed it.

MR. GREGORY: It could have been a combination. I am not sure. EPA probably drove the -- and so they upped theirs to 98.8. So we took the approach that: Hey, we are sitting at the 98.4 percent with our worst case fuel, which is waste coal.

Deseret is now proposing 98.8 for their worst case, which is also waste coal -- their primary fuel.

So we basically said: Okay. We need to maybe look at a 30-day complement to our 24-hour limit, and then in doing that, we probably ought to adjust that 30-day limit to be in sync with the Deseret removal efficiency.

We couldn't match their sulfur.

MR. BUCKHEIT: Well, if they are burning waste coal and we want to burn waste coal here, is there some substantial difference in the

sulfur content for their waste coal?

MR. GREGORY: There is a difference in sulfur content and a difference in heat content, which translates to: They have an inlet S02 concentration of about 4.73 pounds per million BTU, and we have an inlet S02 concentration of 7.3 burning only waste coal.

So that was another reason we said: Okay. If they figure they can get 98.8 percent with that lower inlet S02 concentration, then we ought to try to match it at 7.3.

MR. BUCKHEIT: Thank you.

I now go back to Rob.

Rob, the record is replete with statements, and there have been numbers of statements orally that basically the fuel mix proposed by the company is a given, and we will work from there.

And I think we just heard again that we took a removal efficiency times the fuel mix proposed by the company to derive these limits.

But I thought earlier today you said that you did give consideration to cleaner fuel.

Could you just clear those two apparent conflicts up?

MR. FEAGINS: Well, there is documentation that has been provided to us throughout this lengthy process by the applicant that shows cost analysis of different types of fuels.

And I believe that most of that information has been available to you.

And we did examine that information as part of the follow-on review that we have been doing and.

And we looked at it again as recently as this morning, and we see that the numbers as far as dollars per ton would be out of line if one looked at it in a cost analysis, say with the BACT.

MR. BUCKHEIT: Earlier rationales had said that the department believed that -- I don't know whether it was as a matter the policy or as a matter of law -- that they could not require an applicant to change their fuel mix, that that was the given.

This appears to be a revision of that thinking.

MR. GREGORY: I don't believe it is. I believe we're standing by that, that we do not

believe that we can revise or change the fuel parameter if we did look at it.

MR. BUCKHEIT: Well, here you're saying well, maybe we can, but having looked at the cost figures, we decided not to.

And that is just a different sort of fundamental philosophy, as opposed to we are not authorized to require --

MR. FEAGINS: Well, let me clarify my statement.

We evaluated the alternative fuels after the close of the public comment period, and that information became available to us. And I --

MR. BUCKHEIT: I am just curious as to what the department's current policy is.

Does it believe that it can order cleaner fuels, or does it believe that ordering, for instance, coal washing or something else is redefining the source and therefore not allowed?

MR. BUCKHEIT: That is the position we have taken in our Response to Comments.

MR. BUCKHEIT: The latter.

MR. FEAGINS: The latter.

MR. LANGFORD: Could you briefly summarize those numbers that you said you looked at again this morning for us.

MR. FEAGINS: For which pollutant?

MR. LANGFORD: You talked about the cost numbers that were too high, that you looked at them again in morning.

Are those the cold numbers that were provided in Exhibit 7 to the data that we got in March?

MR. GREGORY: They were provided by Dominion.

MR. FEAGINS: It was provided by Dominion. I believe that is the information.

MR. MOORE: Those are the ones that include reference to points to the .09 percent sulfur coal, .35 percent sulfur coals and .35 percent sulfur coal and some .75 percent sulfur coal.

I'm doing that from memory.

MR. FEAGINS: Well, I can't tell you.

MR. MOORE: But there has only been one submission on that basis; right?

MR. FEAGINS: That I am aware of.

MR. MOORE: Well, if you're not aware of

it, we're in trouble. All right.

MR. FEAGINS: Can you point me to where that is? I don't have know that I have access to that document here.

MR. MOORE: It is Exhibit 7 to Appendix 3 or something.

Wait a minute. I can see if I have got it here.

MR. GREGORY: I believe the cost effectiveness figures that Rob was speaking of also was $12,000 per ton for Powder River Basin coal and 30,000 for simple Appalachian.

MR. MOORE: I don't see that they have the number right here, but was it the one that -- was it the exhibit or attachment -- I think it was maybe Attachment 7 to --

MR. FEAGINS: It is Exhibit 7, Mr. Moore.

MR. MOORE: And it is the attachment to the March 6, 2008 letter?

MR. GREGORY: I believe that is correct.

MR. MOORE: And is it not correct that, you know, the coals that they looked at for comparative purposes were .09 -- do you have it there?

MR. FEAGINS: I have Table 3, which is

the one that we glanced at this morning and it is what Mike Gregory just referred to as the Powder River Basin coal being --

MR. MOORE: There is a summary page where it shows different kinds of coals they looked at.

MR. LANGFORD: Was that provided to us by electronic means?

MR. MOORE: I don't know.

MR. FEAGINS: I don't seem to be able to find the document that you're referring to.

There is a table later in that exhibit, that is a summary of recent BACT, but I don't see the sulfur content numbers that you're referring to.

MR. LANGFORD: Does the company have that?

MS. FAGGERT: We think so.

MR. FEAGINS: On this page, Mr. Moore, I see the S02 reduction.

MR. MOORE: And on the left-hand side they list the various coals they looked at -- Central Appalachian.

MR. FEAGINS: Central Appalachian.

MR. MOORE: At .75.

MR. FEAGINS: The table I am looking at does not have it.
MR. MOORE: And one of them has the -- flip through there -- one of them says what the sulfur content is in each of those examples.
MR. FEAGINS: You may be referring to Table 1, which is Page 3.
MR. MOORE: That may be.
MR. FEAGINS: Okay.
MR. MOORE: But that does summarize it, does it not?
MR. FEAGINS: It does have sulfur contents.
MR. MOORE: Right. And it shows for the -- one of them -- the first one is .75?
MR. FEAGINS: Well, the Southwest project for the Virginia City hybrid energy center blend is first at 2.28 and then Central Appalachia at .75, Powder River Basin is --
MR. MOORE: Well, the first one is the so called base coal, what you are comparing it to.
MR. FEAGINS: Columbia, .68 and Indonesia, .09.
MR. MOORE: Okay. Read those again.
It is .75 -- the ones they are trying to

compare -- .75, right?

MR. FEAGINS: .35, .68, .09.

MR. MOORE: .09. All right. Thank you.

MR. GREGORY: Uh-huh.

MR. LANGFORD: I don't have that kind of a memory.

Is there a way we could get a copy of that reference somewhere?

I haven't found it electronically either.

MR. GREGORY: It looks like Exhibit 7 to Attachment 3 or something like that.

MR. LANGFORD: Attachment 3?

MR. GREGORY: Exhibit 7.

MR. LANGFORD: Table 3 cost effectiveness -- several different versions ranging from $12,900 per ton to $114,000 per ton, based on the -- it looks like it is the cost differential between the cost of alternative coal and that of the Southwest Virginia coal plant.

MS. THOMSON: So this is the difference between Virginia coal versus imported.

Is that what you're looking for?

MR. LANGFORD: Yes, it does appear to be that.

MS. THOMSON: Okay.

MR. LANGFORD: The coals listed are Indonesia, Columbia, PRB, which I believe is Powder River Basin, which is midwest.

All right. And something called CAP, which I am not familiar with.

MR. BUCKHEIT: Central Appalachia.

MR. LANGFORD: Anyway, those are the numbers that I was looking for, Mr. Feagins. I do have them now.

All right. Are you finished?

MR. FEAGINS: I would like to go back just a moment, if I could, to mentioning the document that Cindy handed out.

And at the top it is called, "Revisions to Board Draft," and those are the three areas of revisions that we recognized after we submitted the draft to you.

And one -- the top bullet, at the top, number one, is the revision to the annual limit for particulate matters that we believe is commensurate with the addition of the 30-day limit that we proposed in there.

And that was inadvertently left out. We have done the calculations, and we have

established that limit at 246.92 tons per year, as you can see there in item number one, and then the other two are just housekeeping issues to get the references and wording right so that the compliance monitoring and record keeping and so forth can be coordinated for the 30-day rolling average.

MR. BUCKHEIT: That series of questions is intended to address statements in your Response to Comments, generally to the point that compliance with the MACT means that there is no problem. I am not quoting or paraphrasing here.

You would agree that this region has been in substantial compliance with the S02 secondary MACTs for a long time?

MR. FEAGINS: Yes.

MR. BUCKHEIT: And S02 emissions are largely responsible whatever acidic deposition problems we have in this region today?

MR. FEAGINS: That is consistent with the rules that have been developed by EPA in a number of studies.

MR. BUCKHEIT: So would you agree with me that compliance as to secondary S02 MACTs

doesn't mean that we don't have a problem with respect to acidic deposition in the Southern Appalachians?

MR. FEAGINS: I'm not going to go as far as speculating.

MR. BUCKHEIT: But you said in your response to comments that compliance meant that there wasn't a problem.

You speculated in that direction.

MR. FEAGINS: That's correct.

MR. BUCKHEIT: And you are going to stand by that?

MR. FEAGINS: Yes.

MR. BUCKHEIT: Okay. With respect to PM2.5, that seems to be coming up -- this area is just marginally in attainment with the 15 microgram annual standards; is that correct?

MR. GREGORY: That is correct.

MR. BUCKHEIT: In fact, if we look further east, to say, Fairfax or Arlington, our PM2.5 trends are better.

MR. GREGORY: I'm a little confused at the --

MR. BUCKHEIT: We have cleaner air inside the beltway than in Wise County.

MR. GREGORY: I would not --
MR. BUCKHEIT: With respect to PM2.5.
MR. GREGORY: I would not concur with that statement because that area is --
MR. BUCKHEIT: I am not talking about legalities. I am talking about what I breathe.
The actual measured ambient air concentration, PM2.5, are lower in my part of the state than here.
Is that correct?
MR. GREGORY: I would say the observed data and the modeling that we have conducted does not support that.
MR. BUCKHEIT: How about the observed data?
MR. GREGORY: I don't believe -- the observed data on that --
MR. BUCKHEIT: We'll put that up on the screen later.
MR. GREGORY: I mean, if you're talking about Bristol, Tennessee --
MR. BUCKHEIT: I looked at Roanoke, Bristol, and then there's one in Kentucky and then there is one east.
So I looked at four sites that are

surrounding this place, and I guess we can put it up later.

MR. KISS: Yes. On a daily basis we conduct air quality forecasting, and we look at this information every single day.

And I can tell you that while there are some days in Southwest Virginia that might exceed the standard --

MR. BUCKHEIT: I am talking about an annual average. I am not saying it is over the limit. I am saying it is higher here than in --

MR. KISS: For what period of time?

MR. BUCKHEIT: Annual average -- the trend report shows us the last four years.

MR. KISS: Oh, the trend is upwards?

MR. BUCKHEIT: No, no. I am looking at the trend report data, and I will put it up on the screen this afternoon, but as I looked at it, this area is very very close to non-attainment, right now, based on the trends.

And there is actually more head space where people think the air is dirty, which is in my part of the state.

MR. KISS: I have not done a comparison

of the two.

MR. BUCKHEIT: That is just an issue that I put out to folks is, one, we don't have a lot of room with respect to the EPA published health base standards with respect to PM2.5 emissions in this part of the state.

Would you agree with that?

MR. KISS: Yes.

MR. BUCKHEIT: Okay. It is forecast that the ambient air concentrations in this part of the state, will in fact, go down over the next couple of years; correct?

MR. KISS: That is correct.

MR. BUCKHEIT: A large part of that forecast is premised on EPA's CAIR rule.

Is it not?

Yes. I would agree with that.

MR. BUCKHEIT: Okay. And there is a substantial possibility that in the next month or so, EPA's CAIR rule will be overturned.

MR. KISS: I won't comment on that.

MR. BUCKHEIT: You have heard that?

You are not an attorney. I understand. You have heard that out there.

MR. KISS: I have heard that.

MR. BUCKHEIT: While some companies like Southern Company are pretty far down the road with actually installing controls -- they are pretty far away from us here in Wise. TVA has plans to install controls -- presumably to comply with CAIR.

If the CAIR rule is overturned, and we don't have this here -- my thinking is that Southern Company's units will come online and S02 allowances will get very cheap, so it may not be in TVA's interests to control the power plants that are 100 miles or so from here, the ones that are around Knoxville.

Assuming all that speculation occurs, are our forecasts for defining PM2.5 ambient concentrations in this area at risk?

MR. KISS: I believe if we don't get the reductions from CAIR -- we haven't actually simulated that in the modeling, but that certainly would hinder progress towards lowering those numbers.

In the immediate vicinity, however, there are consent orders in place that are calling for other reductions, so it is not just simply CAIR -- there are some other measures out

there.

Now, whether or not we achieve the reductions that we are talking about in the projections, we probably wouldn't get to that level.

MR. BUCKHEIT: In addition, I assume you are familiar with the letter from CAASAC to EPA respecting the most recent decision on the PM2.5 ambient standard.

MR. KISS: Yes.

MR. BUCKHEIT: And in that letter, the Clean Air Act Science Advisory Comittee, the scientists who served on a Congressional advisory panel to EPA, strongly argue that retaining the current 15 microgram standard is not protective of public health and that that standard should go down for a range of between 13 and 14 micrograms.

Are you familiar with that?

MR. KISS: Yes.

MR. BUCKHEIT: Is it fair to say that since we're sitting today at 14.9 or 14.7 or something like that -- some number well above the 13 or 14 range, that actually based on the science, our air is not fully protected?

It is not as clean as it ought to be here in Wise County today.

MR. KISS: I would rather not speculate on the validity of the MACT standard. We enforce the 15 microgram standard. I understand that the --

MR. BUCKHEIT: But again, come back to whether it is our job here to check the boxes in a federal scheme, or to think about whether we are protecting the public health in Virginia.

MR. KISS: I am going to refer to Mike Dowd for that question.

MR. DOWD: I am Mike Dowd, again the air director.

We enforce our regulations. We implement our regulations. We understand -- we take the regulations -- the duly promulgated regulations to be the embodiment of the state's -- both the board's interpretation of state air pollution control as well as the General Assembly's.

At the moment, the standard that we implement and enforce is the .15 standard.

If and when that standard is changed by EPA, we will take measures to implement and

enforce that standard when it comes.

MR. BUCKHEIT: Thank you.

MS. THOMSON: I have one more question that goes to modeling.

I just want to understand how this was resolved.

In the modeling analysis -- and this must have been based on the original S02 numbers, although they are lower, but not that much lower than previously.

The MACT analysis predicted maximum concentrations that far exceeded the NAAQs -- for, as I am looking at the chart here -- and this was the NPEQ's engineering analysis, PM10, both for the 24-hour, for annual, and for S02, the three-hour, 24-hour and annual limit.

At the same time, in your Response to Comments, you say that having to worry about this facility's causing or contributing to NAAQ's exceedance, that that is not a concern, so I am wondering how you reconciled those two dramatically different sets of results?

MR. KISS: Sure. I guess the first part of that, is that when we do modeling, if we identify a National Ambient Quality Standard

exceedance, we have to determine whether or not the applicant is causing or contributing to that violation.

And there are significance levels laid out to do that type of analysis.

We did that for the Virginia Hybrid Energy Center, and they did not contribute to any of those violations.

We took a further look into those violations, and I will just break it out with taking a look at PM10 first.

Those violations, when we examined them, we determined that those impacts were either on the Carbo plant's property or on Jewell Coke's property, so they were not considered ambient air.

So those exceedances actually went away in the final analysis.

There were sulfur dioxide exceedances identified, and we determined that the AEP Carbo facility and AEP Clinch River facility was the source that was either causing or contributing to those violations.

We have since entered into a consent order to resolve those issues with the plant.

And so, at this time, once that consent order runs its course, we should have resolved those particular issues.

MR. BUCKHEIT: What is the time frame for correcting Carbo?

MR. KISS: The permit, or the final limit would be in place in January of 2009.

MS. THOMSON: I just want to understand the subtleties here with respect to PM10.

MR. KISS: Sure.

MS. THOMSON: So it sounds to me that you are saying that there are real exceedances of PM10 MACTs on Jewell Coke's property and on the Clinch River.

Is that correct?

MR. KISS: Yes. Those exceedances or those concentrations that facilities deal with onsite are dealt with the -- OSHA deals with those -- Occupational Safety and Health Administrion deals with onsite concentration.

They are not considered ambient air because the public does not have access to those areas.

MR. BUCKHEIT: Your modeling, your resolution is so fine that you can establish

that it is inside the fence line?

MR. KISS: Yes. We actually plotted all this information, this geographic information, and you can take a look at it.

MS. THOMSON: So in other words, for those who would be concerned, upon reading this table in the engineering analysis, the response is that under the Clean Air Act, your definition of ambient air -- the Clean Air Act's definition of ambient air -- is air to which public has access to.

So to the extent that you model exceedances of -- or no, for monitoring the exceedances of MACT on company property, those under the Clean Air Act do not count against an exceedance of the National Ambient Air Quality standard.

Is that right?

MR. KISS: That is correct.

Now, you are referring to the concentrations in the report that we had published.

Those particular concentrations -- many of those concentrations in that table were considered ambient air, but with respect to the

AEP Clinch River facility, we have resolved those issues through a consent order.

MS. THOMSON: And just for comparison purposes, we will be talking about different sulfur dioxide emissions from both hybrid energy center, but for those who haven't been able to dig into the comments and so forth, could you just cite for comparison -- and basically what you are saying is that the S02 analysis showed that to the extent to which there were potential exceedances of the S02 MACT, those captured in the Clinch River emissions and not from the hybrid energy center, so could you just tell us what some of the emissions are.

MR. KISS: Sure. I mean, I think Mr. Feagins might have a better handle on this, but in terms of actual emissions in recent years, the Clinch River facility has been upwards of roughly 27 -- 28,000 tons of sulfur dioxide emissions.

There is an EPA consent order or consent agreement that is in place that is going to reduce that number to roughly 16,000 tons by the year 2016.

In comparison, in the facility that we're talking about here, I believe that the limit was roughly 2500 tons of S02.

So considerably less than the Clinch River facility.

And just to clarify the record, I believe there was a question earlier about the increment consumption from the proposed facility, and I did track down those numbers while I was sitting over on the side.

For the three-hour Class One increment, the highest impact on any given day is 5.8 percent of the Class One increment, and for the 24-hour increment, the increment consumption on any given day, the worst-case impact was 8.4 percent.

MR. MOORE: And are all those deemed to be added to the worst-case scenario for everybody?

MR. KISS: No. That is a good point, Mr. Moore.

The highest concentration was 4.58 micrograms per cubic meter on a 24-hour basis.

These are the highest values on any given day. And they don't necessarily coincide with

that maximum impact.

Unfortunately, I do not have the value on that particular day, where that 4.58 value was modeled.

MR. MOORE: So it may or may not have been a greater impact.

MR. KISS: No. It would be no higher than 8.4 percent on any given day. It would be less than that.

MR. LANGFORD: Are we ready to move on to the next presentation?

MR. MOORE: I have some exhibits that I have passed out to you-all, and I would like a few minutes.

MR. LANGFORD: Can that be best done now?

MR. MOORE: Mr. Feagins, I am going to get to this exhibit in a second, but according to the staff, we're really looking at two kinds -- when you're looking at this permit, we are looking at two kinds of fuel -- 1 percent waste fuel with BTU content of about 2738, and the second is run-of-mine coal that has 2.28 percent of sulfur and a BTU content of about the 7782, and blends of those.

Is that correct?

MR. FEAGINS: That very well characterizes the fuels we have evaluated.

MR. MOORE: All right, sir.

And in your presentation, at page 113 and 114, you go through and show the amount of sulfur that is -- and sulfur dioxide that is going into the boiler for three scenarios.

Do you not, sir?

MR. FEAGINS: Yes, sir. I believe we do.

MR. MOORE: Okay. And you do that on an hourly basis. You do it for 100 percent waste coal, 100 percent ROM, and 60 percent waste and 40 percent ROM.

Correct?

MR. FEAGINS: I believe that's correct.

MR. MOORE: All right. What I have done here, so we could get just an order of magnitude of what we're talking about is, I have taken those hourly numbers and assumed a full year.

I understand that it may be unlikely that the company would run waste coal all year, but just to give us an order of magnitude of the tons we are talking about, the S02 -- the sulfur we are talking about and the S02 we are

talking about, I've done that for purposes of the discussion here.

And if you will -- and I gave you this exhibit and you were good enough to point out I made a mistake on one of the numbers and I think you will see I fixed that. I was off by a few tons on one of the numbers.

The first line assumes 100 percent waste coal at 1 percent, and what impacts the number of tons that are burned of course is BTU content.

Right?

MR. FEAGINS: Yes, sir.

MR. MOORE: And with the low BTU content we're talking about, it would take ten million tons of waste coal to operate this facility for an entire year?

MR. FEAGINS: The arithmetic extends to give that number. Yes.

MR. MOORE: All right. And the number two, we have got 60 percent waste and 40 percent ROM and the BTU content there is about 4755.

Right.

MR. FEAGINS: Yes. When I checked your

calculations last night, that is --

MR. MOORE: And it doesn't quite cut it in half, but it reduces it a great deal.

Interestingly, if you put more of the higher sulfur coal in, because it has a higher BTU content, obviously you have less coal -- about a million tons a year less coal.

Right?

MR. FEAGINS: It could work out that way, yes.

MR. MOORE: Well, the math shows it does, doesn't it?

The 47 million compared to -- I think it's 4.7 million compared to 5.7 million?

MR. FEAGINS: Uh-huh. Yes, sir.

MR. MOORE: All right. And then 100 percent ROM coal at 2.28 comes out to about three-and-a-half million.

Now, let's look at the amount of sulfur that goes into the boilers.

As I have it here, the sulfur -- the waste coal would be the highest, and you mentioned that at 100,000 tons of sulfur.

Then if you go 60 percent waste, you are at 87, 84 at 40 percent waste, and all

run-of-mine would be 80,000 tons.

Right?

MR. FEAGINS: Those numbers are correct.

MR. MOORE: Now, interestingly, the last two of those, the 84,000 tons and the 80,000 tons, for perhaps a number of reasons -- but one of the reasons under your rule of the 1.5 percent would prohibit that because both of those are higher than 1.5 percent on average.

Right?

MR. FEAGINS: Yes. Lines three and four do come up to be higher than 1.5 percent.

MR. MOORE: Right. So those two couldn't operate -- the higher two could operate that way?

MR. FEAGINS: If you considered that the fuel blend was that all the time, yes.

MR. MOORE: All right. And you only gave us -- you gave us here three scenarios -- all waste, all ROM, and 60 percent waste, and 40 percent ROM?

Right?

MR. FEAGINS: That's correct.

MR. MOORE: Earlier in the January 7 analysis, you also gave us a different one for

the blend. They are the 60 percent ROM and 40 percent waste.

Right?

MR. FEAGINS: That's correct.

MR. MOORE: I sort of assumed that maybe the reason you flipped that was you couldn't do that all year round.

Was there any reason for changing the scenario?

MR. GREGORY: No. We had simply seen those two different blends presented by -- in different Dominion documents.

MR. FEAGINS: Mr. Gregory said that we had seen those two blends presented in Dominion documents, and we examined both cases.

MR. MOORE: Right. All right.

Now, if one wants to consider coal with both higher BTUs and lower sulfur, we see a fairly dramatic drop in sulfur going into the boiler, do we not?

MR. FEAGINS: If we are looking at lines five and --

MR. MOORE: I am looking at lines five, six and seven.

MR. FEAGINS: Yes.

MR. MOORE: And in each of those cases, because of the higher BTUs, the tons of coal it requires to operate the plant drops dramatically.

Do they not?

MR. FEAGINS: That is correct.

MR. MOORE: And the amount of sulfur drops even more dramatically, so that if we just take line five -- .9 percent sulfur and 12,400 BTU coal, round it to 20,000 tons -- that is a fifth of all waste coal.

Right?

MR. FEAGINS: Your numbers would indicate that.

MR. MOORE: All right. And it continues to go down six -- goes down more because it has both higher BTU and lower sulfur.

Right?

MR. FEAGINS: Yes, sir.

MR. MOORE: And seven goes down even though the BTU content is a little below the other two low sulfur coals, the sulfur content is enough lower to where the sulfur intake is lower.

Correct?

MR. FEAGINS: Correct.
MR. MOORE: Now, as we begin to look at removal efficiencies -- and I am not asking you to agree to a 99 percent removal efficiency, but I am going to do that because it makes the math easier.
If we were to decide we had a 99 percent removal efficiency, then we would have 1 percent of the sulfur dioxide going into the unit available.
Right?
MR. FEAGINS: Yes.
MR. MOORE: All right. And I don't think you're going to need a calculator.
1 percent of 200,000 is 2,000.
If you have got 99 percent efficiency with the waste coal, you would still have 2,000 tons of S02 emitted from the plant; correct?
MR. FEAGINS: That's correct.
MR. MOORE: And line two is 1700, line three is 1600, line 4 is 1600.
So we are at from 1,600 to 2,000 tons a year.
Right?
MR. FEAGINS: According to your

arithmetic on your table, yes.

MR. MOORE: All right. And when we drop to the low sulfur coal, that drops dramatically as well, does it not?

We are now talking about under 400 tons of S02.

If you consider the control efficiency remains constant, yes.

MR. MOORE: Yes. Yes.

All right. That is all I have.

MR. LANGFORD: Are there other questions on the PSD permit?

It is after 11:00 -- in anticipation of numerous questions on the MACT permit, I am going to propose we take a ten minute stretch break, and so we will be back in ten minutes.

(Whereupon, a short recess was taken.)

MR. LANGFORD: The meeting will come to order. I think we have another presentation by staff.

Mr. Dowd.

MR. DOWD: Okay. Good morning. I'm still Mike Dowd, the air director of DEQ, here to speak to you this morning about the proposed MACT permit, for the Virginia City hybrid

energy center.

DEQ made several significant changes from the proposed MACT permit, especially with respect to mercury limit.

The public comments focused very heavily on mercury, and I think that was borne out yesterday. There was very heavy public concern about mercury.

So following the public comment period, we reconsidered the mercury limit and changed it from 49.46 pounds per year, 8.19 pounds per year and a 1.4 times 10 to the minus six pounds of mercury per megawatt hour limit.

The limit is based on a new best control similar source. The permit still requires activated carbon injection, or ACI, which represents beyond-the-floor MACT control for circulating fluidized bed combusters.

And also I want to point out that the limit is not based on mercury content of coal but rather on the best control similar source.

Let me discuss the process we used to determine MACT limits under DEQ's regulations.

A MACT emission limitation means an emission limitation which is not less stringent

than the emission limitation achieved in practice by the best controlled similar source, and which reflects the maximum degree of reduction in emissions that the board, taking into consideration the cost of achieving such an emission reduction and any non air quality health and environmental impacts and energy requirements, determines is achievable by the constructed or reconstructed major source.

Now, DEQ uses a two-step approach in determining that, and that is relatively standard.

First we determine the MACT floor, which is the first provision I read to you.

And then we consider what we can do to go beyond the MACT floor, based on factors contained in the second provision I read to you, and I'll get into that in more detail as we proceed.

But the first step in the process of determining the MACT floor is finding the similar source.

"Similar source" is defined in our regulations as a stationary source or process that has comparable emissions and is

structurally similar in design and capacity to a constructed or reconstructed major source such that the source could be controlled using the same control technology.

Now, based on this definition, DEQ determined that the category of sources most similar to the Wise County project to be circulating fluidized bed or CFB power plants.

Our examination focused on 32 facilities, most of which was CFB, but we did look at some PC or pulverized coal units for comparison purposes.

Based on our analysis, DEQ selected the Reliant Energy Seward Station, located in East Wheatfield Township, Pennsylvania as the best controlled similar source, because they have the lowest demonstrated mercury emission rate, and the best control technology we could find.

I put up a comparison there between Seward -- Seward is a CFB, like the Wise County project. They both have approximately the same megawatt capacity.

Seward burns only waste coal. And that is slightly different than the fuel mix that the Wise County project will use, which has

been proposed to burn waste coal, run-of-mine coal, and biomass.

While not a perfect match with respect to mix of fuels, we still believe that the Seward plant was the best controlled similar source when we looked at all the other sources out there.

First, I wanted to talk about the technology, because that is one of the factors you look at when you consider what the best controlled similar source is.

Seward has a fabric filter to control particulate emissions.

It has a selective non-catalytic reduction to control N0x. It has lime injection as well as a polishing spray dryer to control SO2 emissions.

Similarly, we're going to require the Wise County project to have a fabric filter and SNCR as well as lime injection and a dry fluidized gas desulfurization unit as well.

The technology, in that respect, is very similar to Seward.

We wanted to make sure that the controls match up.

MR. LANGFORD: The "F" in the FGD -- that is normally Flue Gas Desulfurization.

MR. DOWD: It is a typo, yes. There is probably a couple in there.

I'll point out a couple of others. There are one or two others, as we proceed.

I want you to note here that the Virginia City project also has activated carbon injection. We selected that as a beyond-the-floor control for the project.

Seward and no other CFB in operation has activated carbon injection to control mercury -- not any currently operating CFBs.

MR. LANGFORD: Just to reinforce what you just said -- you said that no other CFB that is operating in the country anywhere has got in addition to flue gas desulfurization also the activated carbon injection.

MR. DOWD: That's correct -- based on our research.

MR. LANGFORD: Thank you.

MR. DOWD: That is an additional measure that we're putting on. I'll discuss that in more detail as we go forward.

The primary reason for selecting the

Seward plant as the best controlled similar source were the results of a stack test conducted at the plant in 2006.

The test was performed by the Pennsylvania Department of Environmental Protection using the Ontario-Hydro Test Method, which is the principal test method to test for mercury emissions.

The test however was not for mercury compliance purposes, but rather to study PM emissions.

The test, however was not conducted in strict accordance to prescribed methods -- for example, one example is the test took only 96 minutes.

It is recommended that the test time be two to three hours.

That is just something to take into consideration.

Also it is important to know that the quantification level or the level of applicability -- and those terms are roughly similar in this context -- the level of applicability of the Ontario-Hydro test method is approximately .3 pounds per trillion BTUs.

MR. BUCKHEIT: Mr. Dowd?
MR. DOWD: Yes.
MR. BUCKHEIT: I have not seen any piece of paper or anything that talks about the quantification level of the Ontario method.
Is that in our record?
MR. DOWD: We have looked at the ATSM data --
MR. BUCKHEIT: I understand the applicability reference, but you mentioned quantification.
MR. DOWD: I believe we showed that to you yesterday, Mr. Buckheit.
MR. BUCKHEIT: I think we were looking at the applicability, not quantification.
MR. DOWD: The applicability -- in this case we are going to assume that they are basically similar --
MR. BUCKHEIT: Assuming --
THE REPORTER: I am so sorry, Mr. Buckheit. Your computer is in the way, and I am having --
MR. BUCKHEIT: When an economist is sitting on a desert island, he says, "Assume a light bulb."

MR. DOWD: I didn't catch that, Mr. Buckheit. I'm sorry.

MR. BUCKHEIT: When an economist is stranded on a desert island, he says, "Assume a light bulb."

Okay. I have not seen anything in the record to suggest that the quantification limit for the ASTM method is the same as the applicability limit.

And I am just simply asking you: Do you have anything in the record to support that?

MR. DOWD: No.

MR. BUCKHEIT: Thank you. Let's move on.

MR. DOWD: Now, the Seward test -- the Seward stack test resulted in a result -- came to a result of .02 pounds per trillion BTU and another run -- other two runs came at .01 pounds per trillion BTU.

Now, both -- all the Seward stack test runs therefore were significantly below the stack test applicability level.

Now, what does this mean?

Well, for determining MACT -- well, first I want to point out that one of the steps -- first the MACT floor has been interpreted by

courts to mean the emission control that is achieved in practice by the best controlled similar source under the worst-case foreseeable circumstances.

Well that principal was first brought up in National Lime.

It was articulated in National Lime citing an earlier Sierra Club case. The principle was most recently reaffirmed by the D.C. Circuit in Sierra Club v EPA, the Brick Kiln case in 2007.

So we take that to mean that when we set the MACT floor, we not only take into account stack tests, and the reliability of that stack test, but we have to consider what that stack test means with respect to how the source will perform over the course of a year, because one stack test by itself is really just a snapshot in time.

Based on the fact that the Seward plant tested -- the test results of the Seward plant came out below -- way below the applicability level of the Ontario-Hydro method, we don't believe that there is any test data demonstrating Seward's long term achievability

of a .02 pound per trillion BTU limit.

However, Seward stack tests do tell us two very important things.

First of all, Seward does have very low mercury emissions. They are certainly no higher than .3 pounds per trillion BTU, and the actual rate falls somewhere between .3 pounds per trillion BTU and zero.

To what extent they tested at .02, we think that any result that gets you below .3 pounds per trillion BTU carries with it a great degree of uncertainty.

So taking that uncertainty into consideration, DEQ believes that the presumptive MACT floor for the Wise County plant is the applicability level of approximately .03 pound per trillion BTU.

Now, you don't stop at the MACT floor.

MR. LANGFORD: I think you misread the chart. You said it is .03. I think it is 0.3.

MR. DOWD: 0.3. I'm sorry.

MR. LANGFORD: Just for the record.

MR. DOWD: The chart is correct on that one. That is not a typo. I was in error.

But we didn't set the limit at .03 -- 0.3

pounds per trillion BTU.

We employed the beyond-the-floor MACT measure of requiring installation of Activated Carbon Injection, or ACI, as well as based on the projected performance -- and this is sort of an estimate -- we set the final limit that we are proposing -- well below -- significantly below .3 pounds per trillion BTU.

The proposed mercury limit was set at .149 pounds per trillion BTU, which translates to a number of approximately 1.49 times ten to the minus seven pounds of mercury per million BTU -- that is just if you move over the decimal places.

MR. LANGFORD: I think there is another typo here.

It says 1.4 times ten to the minus six.

MR. DOWD: That is another --

MR. LANGFORD: Yeah. I think it should be ten to the minus seven.

MR. DOWD: It should be ten to the minus seven.

It is seven for the pounds per million BTU. It is six for the megawatt hours.

MR. LANGFORD: Right.

MR. DOWD: When we correct it.

It translates to, when you put it on an output based limit, which the permit contains, 1.4 times ten to the minus six pounds of mercury per megawatt hour.

MR. LANGFORD: I can see that.

MR. DOWD: Which is the rate that is in the proposed permit.

When this rate -- when this emission rate is multiplied by the gross megawatt output of the plant and multiplied by the presumed operating period of a full year, 8760 hours per year, that number translates to 8.19 pounds of mercury a year, which is the annual mercury limit contained in the permit.

We believe this methodology is consistent with the methodology Pennsylvania used to set the mercury limit at the Robinson plant, which has been permitted, but not constructed or in operation.

And that limit was, certainly in part, based, as we have been told by Pennsylvania officials, based on the Seward stack test data.

MR. BUCKHEIT: Is that a MACT limit?

MR. DOWD: It is not a MACT permit.

MR. BUCKHEIT: Is that a MACT limit?
MR. DOWD: A MACT limit?
No it is not a MACT limit. It is not technically a MACT limit. We were told by Pennsylvania staff that when they issued the permit, based on the uncertainty of the camera regulations that they considered the 112-G process in coming up with that number.
So, no, it is not a MACT permit.
MR. BUCKHEIT: It is an allocation from Pennsylvania; right?
MR. DOWD: That is not what we understood from Pennsylvania officials.
MS. KEY: Pennsylvania prepared that number to be a MACT limit, because they weren't sure that the camera regulations were going to be promulgated.
It turns out to be that number is the same as camera would have required. So when camera was promulgated, that limit right now in their permit is in there under authority of camera. They have indicated that they are expecting to go back through the 112-G process and they know of no reason that they will change that number. They expect it to be a

MACT limit.

MR. BUCKHEIT: However the answer to my question is that it is not a MACT limit. It's a trading rule allocation limit.

Correct?

MS. KEY: Currently. Their expectation is to go back through the 112-G process.

MR. BUCKHEIT: For the benefit of those who aren't privy to the last couple of days.

MR. LANGFORD: Margaret, before you leave, could you identify yourself?

MS. KEY: I am Margaret Key with the office of the air permitting program.

MR. BUCKHEIT: For the benefit of those who haven't been privy to the discussion that has gone on the last couple of days, there has been an issue very recently raised respecting the validity of these stack tests, and what they mean.

And so I have had conversations with Joyce Epps, the director of the Pennsylvania, Division of Air Quality and with Greg Parrish, who is the chief of the original --

THE REPORTER: Speak up.

MR. BUCKHEIT: At the same time, DEQ

staff have been having conversations apparently with other members of Pennsylvania and we have somewhat different statements coming from Pennsylvania to each of us as to what these things mean.

MR. DOWD: Okay. Now, we prepared this chart, to sort of put things visually in perspective.

The line at the top is -- represents .3 pounds per trillion BTU.

MR. BUCKHEIT: And that is mislabeled "quantification level;" is it not?

MR. DOWD: You know, "mislabeled" is --

MR. BUCKHEIT: Did Seward have an applicability level?

Do you know?

MR. DOWD: The difference between "applicability level" and "quantification level" here, is --

MR. BUCKHEIT: -- itself is an applicability level?

MR. DOWD: That is what it calls itself. Correct.

MR. BUCKHEIT: Thank you.

MR. DOWD: In effect it works as a

quantification level because we do have a very low degree of uncertainty as to --

MR. BUCKHEIT: Again, you have nothing in the record respecting a difference between a quantification level and an applicability level with respect to this ASTM limit?

Correct?

MR. DOWD: I don't know.

MR. BUCKHEIT: You don't know if there's something in the record?

MR. DOWD: The ASTM -- it depends on how you wish to interpret an --

MR. BUCKHEIT: No. The question is whether there is something in the record --

MR. DOWD: That actually calls the applicability level of --

MR. BUCKHEIT: That discusses all of this.

MR. DOWD: It does not specifically call it a "quantification level."

MR. BUCKHEIT: And there is nothing in the record that discusses these things.

It is a small point.

MR. DOWD: Our record does contain questions -- our Response to Comments do

contain questions raised about the validity --
MR. BUCKHEIT: Yes, and --
MR. DOWD: -- at this low level and --
MR. BUCKHEIT: I understand that. I am only talking about the word "quantification level."
MR. DOWD: Have it your way.
MR. BUCKHEIT: Well, please answer the question.
MR. DOWD: We can call it an applicability level.
MR. BUCKHEIT: And there in nothing in the record reflecting the difference between an applicability level and a quantification level.
Correct?
MR. DOWD: As to what the difference is between an applicability level and a quantification level?
MR. BUCKHEIT: That's right. There is no discussion or --
MR. DOWD: There is no discussion as to the technical differences between an applicability level and a quantification level.
MR. BUCKHEIT: Thank you.
MR. DOWD: Correct.

Be that as it as may, there is -- whether it is a quantification level or an applicability level, the practical effect is that below that level, any stack test results have a high degree of uncertainty attached to it.

I do want to add that besides a testing conducted by the Pennsylvania DEP, we have been told that Reliant simultaneously conducted some sorbent trap tests that showed an emission rate of .03 pounds of mercury per trillion BTU, which is also quite a bit below the level of applicability.

MR. BUCKHEIT: That is reflected in the Pennsylvania documents, is it not?

MR. DOWD: It is reflected.

MR. BUCKHEIT: It has not just been told.

MR. DOWD: Well, to us, it is just -- if I can go on.

MR. BUCKHEIT: But you read it.

MR. DOWD: We have read it. We have not seen the results of the test.

We have not been privy to them. We have not been given the results of the test. We're unsure whether Pennsylvania has actually seen

these.

MR. BUCKHEIT: Excuse me. But you saw in a document created by Pennsylvania -- Pennsylvania reported --

MR. DOWD: They reported --

MR. BUCKHEIT: -- these test results.

MR. LANGFORD: Just to be clear, that the final number, one number was reported, the department does not have and has not seen the actual test report that would have the data and additional information about it.

MR. BUCKHEIT: I would agree that this department -- Virginia hasn't seen it.

What I think Mr. Dowd said was that Pennsylvania hasn't seen it.

MR. DOWD: I don't know whether they have seen it or not.

MR. BUCKHEIT: But I think you said that Pennsylvania said that.

MR. DOWD: Pennsylvania said that they had -- that Reliant had done some sorbent trap testing.

MR. BUCKHEIT: It was simultaneous --

MR. DOWD: We don't know --

MR. BUCKHEIT: -- testing done at the

same time that Pennsylvania was conducting its testing and in a coordinated matter.

Is that correct?

MR. DOWD: That is what we understand from the Pennsylvania report.

MR. BUCKHEIT: Okay.

MR. DOWD: We don't know if Pennsylvania saw that report, other than just being told about it by --

MR. BUCKHEIT: In the Pennsylvania summary, Pennsylvania reports the results of the simultaneous testing conducted by the industry?

MR. DOWD: Yes, it does.

MR. BUCKHEIT: And Pennsylvania also reports that the simultaneous testing conducted by the industry -- and I'm not sure whether it is one additional test method being used or two additional test methods being used, but the testing conducted by the source was not using the Ontario-Hydro method.

Correct?

MR. DOWD: They use the absorbent track method.

MR. BUCKHEIT: -- method; right?

MR. DOWD: That is what we understand.
MR. BUCKHEIT: And we don't know anything about the protection levels, the quantification levels or the applicability levels of the test procedures used by the company.
MR. DOWD: That is correct. We don't.
MR. BUCKHEIT: What we know is that the company did simultaneous testing using either one or two different methods, and came up with roughly the same results in the 02 range.
When I spoke to Joyce Epps, the director of Air Quality, and the testing chief, and asked them since this was a controversial subject, were they standing by their numbers, they said yes, they were.
MR. LANGFORD: I am trying to also make the record clear -- the report from Pennsylvania again has a single final number in it and the department does not have information and is not aware of whether Pennsylvania's department has information regarding the specific number of runs and the variability of the runs with that test method.
We have a single number.
MR. BUCKHEIT: Well, actually that is

close to correct, but no.

In the test report, they only calculate hours -- a single pounds per million BTU, result but there are two numbers of pounds per hour collected during the test.

MR. LANGFORD: Okay. Move on.

MR. DOWD: An alternative method to the one proposed by DEQ here would be to use absorbent trap test results and apply a safety factor as recently recommended in NACAA's model rule for establishing the MACT for industrial and commercial and institutional boilers.

And when you do the math on that factoring in a -- factoring in as the proposed NACAA model would, a rate of variability -- when you do all the math that rate will come up to about 5.1 pounds a year.

And that is an alternative.

However, due to the uncertainties in sorbent trap testing, as well the Ontario-Hydro method, DEQ staff is still comfortable with the emission limits in the proposed permit.

MR. BUCKHEIT: The 5.14 -- is that 100 percent utilization?

MR. DOWD: Yes. Staff is telling me yes

-- which would be 8760.

I wanted to say a few words about coal washing and MACT.

DEQ did not require coal washing as a MACT floor measure, because it was not used by the best controlled similar source, which was Seward.

Moreover, DEQ did not consider it a beyond-the-floor of MACT measure because we did not believe it met the regulatory definition to be a beyond-the-floor measure.

First of all, we believe that coal washing provides speculative mercury removal benefits.

DEQ could not determine what washed coal -- how washed coal, to what extent washed coal would actually lower mercury emissions beyond those proposed in the permit.

Second, coal washing is basically incompatible with the proposed project.

The CFB -- and the reason for that -- and I think Mike Gregory and --

MR. BUCKHEIT: ACI.

MR. DOWD: Excuse me.

MR. BUCKHEIT: I think you meant to say

"ACI."

MR. DOWD: Did I say "ACI?

MR. BUCKHEIT: No. You said coal washing.

MR. DOWD: Well, coal washing is basically incompatible.

MR. BUCKHEIT: Incompatible.

MR. DOWD: Incompatible. Yes. I thought that is what I said. Incompatible with the proposed project.

CFBs require a constant stream of -- basically a fluidized bed, and it relies on a heavy ash content in its fuel feed.

And to the extent you wash coal you remove that, and to some extent you might have to reinject it at some point.

I am not going to say that coal washing is exclusively incompatible with the project but it is a fact to be considered.

MR. BUCKHEIT: Aren't there CFBs that burn prepped coal?

MR. DOWD: Yes. Thre are CFBs that could be constructed to burn washed coal, as I understand it.

MR. BUCKHEIT: But -- with the notion

that it relies heavily on ash content.

MR. DOWD: I believe that this one does.

MR. BUCKHEIT: This design -- I am just -- as a general statement I am surprised to hear you say it.

MR. DOWD: Well, Dominion may speak more to it in their comments.

I guess very significantly, coal washing is extremely costly for each pound of mercury removed.

Now Dominion told us that coal washing costs approximately 2.5 million dollars for each pound of mercury removed.

Now, even if you wanted to discount what Dominion says and even at one-twentieth -- even at one-twentieth of that cost, coal washing is still highly cost ineffective.

MR. BUCKHEIT: In my April letter -- memo to you-all, I asked folks to go out to coal-washing facilities and simply asking what does it cost?

I didn't see that in the written documentation. I asked the CEO of a coal-washing company and was advised that it cost between three and seven dollars a ton.

Mr. Moore asked the same question and his authorities told him between three to eight dollars a ton on an after-tonnage measure basis, and a dollar to a dollar and a half a ton on an incoming-tonnage basis.

So if you have the 800,000 tons a year coming in and 400,000 tons that are going out, so the cost is double if you measure that afterwards on a per ton basis.

Neither of those numbers sound anything like Dominion's numbers.

Did DEQ conduct an independent examination of this?

MR. DOWD: Not to any great extent, no.

MR. BUCKHEIT: Thank you.

MR. PAYLOR: Let me make sure I understand that.

I thought I understood your number to be cost per pound removed, and I understood the answer that we got to be per ton of coal washed.

MR. BUCKHEIT: Mike's per ton of coal washed was based on numbers provided by Dominion as to the price of different coals from different places.

And I asked about the cost of taking local coal and washing it as opposed to --

MR. PAYLOR: The numbers that I thought I heard you mention, Mike, was cost per pound of --

MR. DOWD: It is cost per pound of mercury removed, not the cost per ton of coal washed. No.

It's the cost of the environmental data --

MR. BUCKHEIT: But that cost is based on a price differential provided by Dominion of coal -- washed versus unwashed.

Correct?

MR. DOWD: Yes.

Coal washing eliminates, in our view, the non air quality benefits of removing gob piles and reducing the creation of new gob piles by burning run-of-mine coal.

And finally, from an energy perspective coal washing reduces the available BTUs by not using all the available BTUs in gob or run-of-mine coal.

For these reasons, DEQ didn't believe that coal washing satisfied the regulations

test to be a beyond-the-floor MACT measure.

MR. BUCKHEIT: Excuse me, Mike.

If you wash coal waste -- okay -- so that you reduce the ash content, don't you increase the available BTUs?

MR. DOWD: You wash BTUs out of coal.

MR. BUCKHEIT: The BTUs per ton going into the unit go up.

MR. DOWD: The BTUs going into the unit go up, yes, but you're using all the BTUs available to society -- when you wash coal, you are throwing away BTUs into the environment that this plant will reclaim by using run-of-mine coal.

MR. BUCKHEIT: The question is: Is there ever a balance when the adverse air emissions are such that you don't go to that next step -- and that was all we're looking at.

MR. DOWD: No -- and I understand that, and balanced out with the first point I made that the benefits of coal washing to mercury removal are very speculative here --

MR. BUCKHEIT: But I hope I don't hear you say that we have to go find every last scrap of coal no matter what it is co-bound

with because we have to have coal.

MR. DOWD: No.

MR. BUCKHEIT: I mean we have lots of high quality coal in Virginia -- in this region.

MR. DOWD: Right. But when we do a beyond-the-floor MACT analysis, we do have to look at energy impacts.

And one energy impact here is that when run-of-mine coal and gob are burned, we're using BTUs that would otherwise be discarded or that had been discarded on a wide range of -- you know that had been discarded in the past, so in a sense it is a conservation of energy measure.

And that's all I am saying.

MR. BUCKHEIT: Well, another question that I also asked, and I don't think I saw an answer to is: Within the regulatory framework, on the RCRA side, the agencies have settled in on a BTU content, when you're thinking about it as a fuel as opposed to just getting rid of the waste, and at some point it seems that this project may have morphed from a hybrid energy biomass project to a solid waste disposal

project.

If you take 2,000 BTU material and try to extract it and transport it and move it along, you may wind up with a net energy loss, in terms of the energy that it takes to take it, move it, and burn it because it is not contributing significantly in the combustion process.

And that is what the boiler industrial furnace rules -- good rules, under RCRA, suggest.

And I asked folks to look at that, and I don't think I saw an answer, but maybe I missed it.

MR. DOWD: It is very hard to calculate. If you're shipping in gob from Kansas, yeah. You are probably burning more --

MR. BUCKHEIT: -- calculation here as to what the floor might be, if it's beneficial in terms of even energy.

MR. DOWD: But this is beyond that.

MR. BUCKHEIT: I see your point.

MR. DOWD: But we are not looking at this as a floor MACT measure. This is a beyond-the-floor MACT measure.

You know, we have got to balance them all together. I mentioned a speculative benefit from washing coal with respect to mercury reduction.

What I understand of the nature of mercury in Virginia coal is that mercury is more bound up in the coal itself than can be washed away.

MR. BUCKHEIT: And I accept that, but I also attended the department's mercury conference last year where there was a presentation that suggested that coal washing was of extraordinary benefit in terms of both sulfur removal and mercury removal.

MR. DOWD: I guess we would have to respectfully disagree with a lot of conclusions of that report. It was a very optimistic report, but it hasn't been borne out by our staff.

MS. THOMSON: Just one point --

MR. DOWD: Yes, Ms. Thomson.

MS. THOMSON: -- of clarification here.

When we were talking about the PSD permit, I quoted the language on the definition of Best Available Control Technology, which

actually bears some striking similarity to MACT, in the sense that there is a clause in BACT that BACT is determined taking into account energy, environmental and economic impact and other costs.

Here similarly, slightly different language, beyond-the-floor MACT, you're supposed to consider non air quality health and environmental impact, and that is why you have specifically identified here the non air quality benefits of removing gob piles.

Is that correct?

MR. DOWD: That's correct. Yes.

But there are some significant differences between BACT and MACT.

Before you even get to considering costs or non air quality benefits --

MS. THOMSON: I am not saying that the emission limitations would be the same.

I'm saying that accounting for those kinds of impacts is clearly both in the definition of BACT and in MACT.

And I just wanted to -- since we have been talking about non air quality related impact as a category of things to be concerned

about and to take into consideration, I just wanted to clarify, for those who are not familiar perhaps with the MACT process that that is why you have identified this here.

MR. DOWD: Well, that's correct and I think the point of clarification is in order -- we cannot take any of these factors into account to reduce what the level would be from the best controlled similar source.

MS. THOMSON: Increase it.

MR. DOWD: Only make it more stringent. That's correct.

MS. THOMSON: More stringent.

MR. DOWD: That's correct.

MS. THOMSON: Okay.

MR. DOWD: But by the same token, if we have to consider -- when we are considering a piece of add-on technology or control, those can be factors -- cost and non air quality benefits can be factored in excluding that from a beyond-the-floor control measure, if that makes sense.

MR. BUCKHEIT: If I can just back you up for a second.

What I am hearing, is you-all have

settled in on the limit imposed by Pennsylvania that I talked about as a mercury trading limit, as the MACT floor.

And the Seward facility doesn't have ACI. Right?

MR. DOWD: It hasn't what?

MR. BUCKHEIT: It does not have ACI -- activated carbon injection.

MR. DOWD: No, it does not.

MR. BUCKHEIT: And a beyond-the-floor requirement, you-all are suggesting that you don't have to measure that.

It seems to me that if the MACT floor is something related to Seward and Seward doesn't have ACI, and you-all have settled in on the Robertson limit as something that represents Seward, then we should expect some additional further reductions from the application of ACI.

MR. DOWD: I will get back to the uncertainty -- Margaret wants --

MS. KEY: I think during the PSD permitting process, there were considerations of whether to require ACI.

And honestly, at this point, it is so early in the process at any one time, that

technology. There is really no demonstration that with the ACI we will get a lower limit.

It is hoped that we can get lower emissions.

There is no good demonstration that we will.

Dominion fought that pretty hard in the PSD process, and in that initially proposed PSD permit, the approach that the department took was to require a limit and say, "If you can't meet it, then you're going have to put on ACI and we will see if that will help you meet it."

In the MACT application, Dominion applied to put on ACI, I think in the hopes that they would be able to get to see through the process more quickly if they volunteered that, but I don't have evidence that ACI controls --

MR. BUCKHEIT: Let me offer this comment: I think that the suite of controls that Dominion has offered here is not a problem.

I think Dominion has offered a suite of controls that quite frankly, is very good and the issue is whether the permit limit reflects the true performance of these devices.

So here we go, you know, activated carbon

injection is generally thought to get you 90 percent removal in most situations and you have a fabric filter there.

I would agree that there is some question as to whether you can get that number when you go down to these very low numbers, but I would have to think that if you take the Seward unit, testing very low, three different methods, and you add activated carbon to it -- okay -- to go an order of magnitude above the Seward results -- I have concerns about that.

MR. DOWD: You believe that there is an inherent uncertainty with any number, any stack test number below the .3 pounds per trillion BTU?

MR. BUCKHEIT: But we have two other methods, with lower detection limits, that we know were used. We don't know the details of it. We know that they were used, and we know the results we get out of it.

So you are ignoring those other two methods.

MR. DOWD: No. We are not ignoring those other two methods at all.

MR. BUCKHEIT: Okay.

MR. DOWD: First of all, the other method that they were doing in conjunction with the other stack test method is being done to calibrate it, and that is the Ontario-Hydro method.

The sorbent trap -- is that not correct?

MR. BUCKHEIT: No, no. Go ahead.

MR. DOWD: The sorbent trap method -- we just -- it's a very complicated procedure to run, and one of the issues with respect to doing a sorbent trap, is sort of having some ballpark idea of what is going to be coming out of the stack.

So -- and that relates to what your run times are on the sorbent trap.

We're just saying that we have no real basis for concluding a MACT floor number above .3 pounds per trillion BTU. That is all we're saying.

MR. BUCKHEIT: You're saying you have no basis --

MR. DOWD: We can't quantify it.

MR. BUCKHEIT: You have no basis -- but put the Ontario method aside.

First of all, you said that you

discounted it because it wasn't for compliance purposes.

MR. DOWD: We didn't discount the test. We didn't discount the test.

MR. BUCKHEIT: It was in one of your bullets -- right?

Well, in the MACT world, where you're setting limits for the for first time for things like cadmium and chromium and beryllium and 198 different MACT pollutants, you are never going to be testing for compliance. There are no standards.

MR. DOWD: But the point is that they weren't testing for compliance.

MR. BUCKHEIT: Right. What they said they were testing for -- okay -- let's see if I can find this here.

They were testing to set emissions -- let me see if I can find it -- emission factors for mercury emissions from these type of units.

It was to be used in the regulatory process -- not for enforcement, but to set standards in permits as we are doing here today.

So help me with what the problem is.

MR. LANGFORD: I haven't seen a problem.
I mean they have said their position and you have said yours.
MR. BUCKHEIT: No, why if DEQ sees it as a problem, why is it noteworthy to say that it wasn't for compliance purposes, if it is intended for purposes of setting standards of permits?
MR. DOWD: The problem is with the applicability level.
MR. BUCKHEIT: No, no. Let's stay here.
You-all had a bullet that it wasn't done for compliance purposes.
What is the relevance of that?
MR. DOWD: Because it wasn't done according to the stack method --
MR. BUCKHEIT: That was a different -- you said it wasn't --
MR. DOWD: It's the same thing.
MR. BUCKHEIT: You said it wasn't done for compliance purposes.
MR. DOWD: No, it was not. It was not done to the rigor of how an Ontario-Hydro method test --
MR. BUCKHEIT: That is a different issue.

We have discussed the AMPM issue somewhat.

I am just tossing on the point of that somehow it is important because --

MR. DOWD: We have seen this issue very different than the issue that it wasn't performed in accordance with rigorous methods. Even if the Ontario-Hydro testing was --

MR. BUCKHEIT: Don't you use --

THE REPORTER: Excuse me. I'm going to have to ask the two of you not to speak on top of each other. Wait for the other to finish.

Otherwise, I cannot make an accurate record.

MR. BUCKHEIT: Don't people use -- isn't it important to use scientific methods for setting permits and setting rules?

Isn't it more important?

MR. DOWD: All I'm saying is that the applicability level --

MR. BUCKHEIT: I am back to your bullet about it.

MR. LANGFORD: Mr. Buckheit, I think you are beating a dead horse. They made their position, you made your position.

I would like Mr. Dowd to go ahead and finish his presentation.

MS. THOMSON: I'm sorry. I just have one, I think simple related question.

I understood Ms. Key to say that the actual effectiveness of ACI in reducing mercury is still a little bit in question.

MR. DOWD: Yes.

MS. THOMSON: Okay. Is it not the case that if, for example, we set -- wherever we set the permit limit -- wherever it is, that if it turns out that after Dominion commences operations in the case that we decide to grant the permit with some set limit in it, that if Dominion finds that it is not achievable with the controls that are in place, that Dominion could come back to DEQ and present that evidence and ask for a different limit.

Is that not the case?

MS. KEY: We do have that provision in the proposed permit. It would not be a simple process for them to do that. They would basically go back through the same process we have been through with this permit.

So --

MS. THOMSON: Notice and comment and all that?
MS. KEY: Notice and comment and all that.
MS. THOMSON: But it is still possible for that to happen?
MS. KEY: It is possible.
MS. THOMSON: You have made provision for that, with full public hearing and so forth.
MS. KEY: Yes.
MS. THOMSON: Okay. So we have that little escape clause there in case we make a mistake about how much removal efficiency we can get here.
MS. KEY: That is correct.
MS. THOMSON: Thank you.
MR. BUCKHEIT: Mike, you-all in your papers mentioned that you needed to assure setting a limit that facilities could meet the limit for -- paraphrasing here -- the useful life of the facility.
MR. DOWD: Did we use that phrase?
MR. BUCKHEIT: I think you did.
MR. DOWD: Well --
MR. BUCKHEIT: I don't recall anything in

the statute that says it even has to be achievable by the facility on day one, much less for fifty years.

MR. LANGFORD: That doesn't --

MR. BUCKHEIT: -- if the staff agrees.

MR. DOWD: I think I understand your question.

And the plant will have to meet the standards of the best performing similar source.

If the best performing similar source actually performs at a level, and we can prove it actually performs at a certain level, then this plant is bound by that, regardless of whether they can meet that actual number or not. I think that's what you're getting at.

MR. BUCKHEIT: You agree with me on that.

MR. DOWD: Yes.

MR. BUCKHEIT: Okay. But then, you-all had a statement that you have a set limit taking into account, that the facility somehow would degrade in performance over its lifetime.

And I've never seen that. Well maintained pollution control devices do not decay in performance to my knowledge.

You-all have a different view on that?

MR. DOWD: No. I don't think so. We would approach it, as, you know, how it would perform over the long term. I am not quite sure about the language about the life in the facility.

MR. BUCKHEIT: There was a comment in there that in setting the uncertainty factor, you had to consider that this unit had to meet over its useful life, and somehow it was suggested that you had to increase the limit -- and again, I've just never seen that -- I mean 30-year-old -- S02 control devices that were built 30 years ago still perform at the level that they were built then.

I have not seen any data that suggests that there is an age factor with well maintained units.

I'm just not getting that.

MR. DOWD: I don't disagree with that, Mr. Buckheit.

MR. LANGFORD: Let's try again for you to move on with your presentation.

MR. DOWD: Okay. Well, moving on. Time to move on to a range of other hazardous

pollutants, other than mercury.

MR. MOORE: Mr. Dowd, let me ask -- the limit for mercury is stated in pounds per million BTUs is 1.49 times ten to the minus seven.

MR. DOWD: That is pounds per million BTU. Now, that is not in the -- the number that -- that translates to the 1.49 times ten to the minus six pounds of mercury per megawatt hour.

MR. MOORE: Your slide ten should have 1.49 as -- it has a zero, but I think it would be 1.49 times ten to the minus seven pounds of mercury per million BTUs -- slide seven.

MS. THOMPSON: Yes, sir. This is Tamera Thompson, director of permitting, DEQ.

Yes, sir. That is correct.

MR. MOORE: Okay.

MS. THOMPSON: It is 1.49 times ten to the minus seven pounds per million BTU, and it is 1.49 times ten to the minus six pounds per megawatt hour.

MR. MOORE: The only question -- I just wanted to make sure I had that number right.

MS. THOMPSON: Yes, sir. That is right.

MR. MOORE: Mr. Chairman, I am going to ask more question -- a preliminary question.
MR. LANGFORD: I have a clarification on her answer to your first question.
MR. MOORE: All right.
MR. LANGFORD: Twice it was stated that .149 pounds per trillion BTU equated to 1.49 pounds of mercury per megawatt hour, but the slide does not have the nine.
MS. THOMPSON: I'm sorry. It is 1.4. I'm sorry.
MR. LANGFORD: You said that. I believe Mr. Dowd said -- it's 1.4.
MS. THOMPSON. Yes. It's 1.4. I'm sorry. What is on the slide is correct.
MR. BUCKHEIT: That's assuming that he --
MS. THOMPSON: Yes, sir.
MR. BUCKHEIT: 500 -- something.
MS. THOMPSON: Yes, sir.
MR. MOORE: Am I correct -- I'm looking at the data for mercury emissions for 2002, which I think are the latest data that we have. And I just want to make sure I am right about this.
Mecklenburg had emissions -- mercury

emissions of 1.35 -- a little below that, in their -- well, 1.35 and 1.46 in 2002.

MS. THOMSON: What are the units? I'm sorry, Mr. Moore.

MR. MOORE: 1.35 and 1.46 times ten to the minus seven.

So I think they are comparable pounds per million BTUs.

MR. DOWD: Yes, I believe so. Doris McLeod will speak to this.

MR. MOORE: I am not saying that's a reason to do this. I am simply pointing out that for the permit, that is correct.

MS. McCLEOD: My name is Doris McCleod. I am the air quality planner for Virginia DEQ.

Yes. That is correct. The Mecklenburg pounds per trillion BTU number is slightly lower in pounds per megawatt hour is slightly higher, based on the 2002 data.

MR. MOORE: Right. Thank you.

MR. BUCKHEIT: So if we were to conclude that Mecklenburg was a similar source --

MS. McCLEOD: Mecklenburg is a spreader stoker.

MR. BUCKHEIT: I understand. But the

definition of similar source is one that can be controlled by similar pollution control devices.

If we were to conclude that Mecklenburg is a similar source, which I haven't, then we would have to reduce the MACT floor to meet Mecklenburg.

Is that right?

MS. McCLEOD: I think it depends on which unit you look at.

MR. MOORE: Well, both of them are a little lower. 2002 -- if those data are correct 1.35, as Mr. Buckheit has asked questions on -- I was going to ask if this had been one of the units in your world, it would have been -- it might have helped set the floor?

MS. McCLEOD: Mecklenburg is between 1.3 and 1.4 times ten to the minus seven pounds per million BTU. That's slightly lower.

MR. MOORE: That was my point.

MS. McCLEOD: But that is not the only point though, if you look at pounds per megawatt.

MR. MOORE: I understand that, and I

don't know whether what -- and I don't know whether you look at that and say: You know, we are going to consider both whether you can look at pounds per million BTU and set it on that or if you have to have a unit that is more efficient.

Obviously, it will do even better -- if it is less efficient, it will be worse.

I was just pointing that out and was going to ask if that was considered in your deliberations?

MS. McLEOD: I do not believe that it was considered, because were looking at CFBs.

MR. MOORE: You were looking at CFBs and this is not.

MS. McLEOD: Yes, sir.

MR. MOORE: All right. Thank you.

MR. LANGFORD: We'll try again, Mr. Dowd.

MR. DOWD: Okay. Well, let's -- we have talked an awful lot about mercury.

Let's turn to some of the other hazardous air pollutants that are addressed in this permit besides mercury.

The other hazardous air pollutants include hydrogen chloride, which was also used

as a surrogate for the non-organic, non-metallic HAPS such as acid gases.

We looked at hydrogen chloride. We looked at hazardous metals. And the hazardous metals -- we used PM as a surrogate for those.

And finally, we looked at organic HAPS, for which we used VOC and the CO limits as surrogates.

MR. BUCKHEIT: CO limits?

MR. DOWD: CO as the surrogate.

MS. THOMSON: Of course, there is a host of pollutants listed as hazardous air pollutants under Section 112 -- 50 or 60, actually, I think that are emitted from coal fired power plants.

So that is the importance in having confidence in the surrogate controls to get down to good emission goal emission level in such toxins like arsenic and cadmium, chromium and so forth.

The one that I'm not quite sure where the co-control comes in, in which you are going to enlighten me here is radionuclides.

MR. DOWD: We don't have authority to regulate radionuclides.

MS. THOMSON: Radionuclides are a section 112 pollutant.

MS. THOMPSON: Yes, ma'am, they are, but EPA has retained authority to regulate radionuclides and we have no authority to look at them.

MR. BUCKHEIT: So is EPA going to do that?

MS. THOMPSON: I have no idea, but they -- we are not delegated to look at them.

They have opted to keep delegation of that pollutant.

MR. LANGFORD: Do you know how --

MR. BUCKHEIT: Do they issue some permit for these plant people?

MS. THOMPSON: Not to my understanding.

MR. LANGFORD: Ms. Thompson, to your knowledge, has EPA ever regulated radionuclides that come out of a coal-fired power plant?

MS. THOMPSON: No, sir.

MR. LANGFORD: Thank you.

MS. THOMSON: So in other words, when we think about the residual RIF here, through no fault of DEQ's own, we have to put radionuclides in an unaddressed category.

Is that correct?

MS. THOMPSON: That is correct.

MR. DOWD: First looking at hydrogen chloride.

Hydrogen chloride is controlled by limestone injection.

It is important to note that here the Seward plant has no HCl limit, and there is no stack test data for that as far as we know.

Our HCl limit is higher than some facilities, but within the same order of magnitude, and it is important to know the key thing here is that the Wise project HCl limit is as stringent as any operating CFB.

MR. BUCKHEIT: Well, here you go.

Several times we have heard you rely on a permit limit for facilities that have not yet been constructed. And I think that is entirely appropriate and consistent with the practice over the decades.

Help me with why we can ignore lower permit limits that have been set by sister agencies after careful examination.

Unless you have gone through them, and I understand you have made error.

MR. DOWD: No. That is a good question.
And first of all, I want to get back to that Reliant and the HCl limits.
So the best controlled similar source, which we are required to look at -- you know, we couldn't use that as a basis of comparison, because they didn't have one.
MR. BUCKHEIT: I mean, what about AES Puerto Rico?
MR. DOWD: Let's turn to that.
Now, let me just mention for a second why -- to answer your question, Mr. Buckheit, directly why an HCl limit might not necessarily be a bad thing -- keeping in mind that the limit we have is as low as any of the other units in our source category.
MR. BUCKHEIT: Let me -- just a brief interruption.
Looking at the acid gas control technology that Dominion has offered -- this is a very high performing system.
I mean, I don't know anything in the country, anywhere in the country where anybody has offered to put on better controls than Dominion has offered to put on here.

So it's not -- again it is not a control issue. It's -- I asked the question earlier on: Is this the project or is it the permit.

And we have a good acid gas controls.

I'm pressing for a rationale why we don't have good limits.

MR. DOWD: The rationale is right here.

MR. BUCKHEIT: Okay.

MR. DOWD: There is direct tradeoffs between HCl and mercury.

There is a relationship between chlorine and mercury.

The chart here -- and I am not a really good one to describe it, but what it shows is the amount of mercury removal -- mercury removal goes up as the chlorine content in the coal goes up.

Clearly, mercury is a pollutant of much greater concern than hydrogen chloride. I think that was brought up yesterday -- Mr. Cruikshank and many other commenters --

MR. BUCKHEIT: I'll give you that.

MR. DOWD: What is important to note is that facilities with lower HCl limits have significantly higher mercury limits.

And, you know, for the sake of comparison, our -- the mercury limit at Wise County is .0066 pounds per million BTU.

Spurlock 4, which has been permitted but is not yet in operation, has an HCl limit half that.

MR. BUCKHEIT: But again, you're saying: I am going to rely on this permit limit, but I'm not going to look at that other permit limit.

MR. DOWD: Which other permit limit?

MR. BUCKHEIT: You said in the record there were several facilities with lower permitted HCl limit, that you're not going to consider, but now in justifying it, you rely on the permit for yet another facility that has not yet been built.

MR. DOWD: Saying we didn't consider it and saying we didn't pick it --

MR. BUCKHEIT: A fair point.

MR. DOWD: We did consider it.

And in the case of Spurlock, which has not yet been in operation -- so we don't know if they can actually achieve the .0035, but take it -- assume that they can, because there

are some low limits out there.
And that also is CFB.
MR. BUCKHEIT: Did Spurlock go through a MACT process?
MR. DOWD: No, it did not. It did not go through the MACT process.
MR. BUCKHEIT: So you don't have the MACT limit for mercury.
MR. DOWD: No, we don't.
But the emission rate at Spurlock for mercury, even though it is not a MACT permit is still an order of magnitude higher.
MR. BUCKHEIT: If you were doing just a BACT permit for this facility, you-all came in at 49 pounds -- or 72 pounds.
So this is Kentucky.
MR. DOWD: Spurlock is.
MR. BUCKHEIT: Yes. So they are only doing BACT and they only do 50.
I don't know what they are telling us.
MR. GREGORY: That's one unit.
MR. DOWD: Mr. Gregory informed me that that 50-pound a year limit --
MR. GREGORY: Half the size of ours.
MR. BUCKHEIT: You know, I am not

defending Kentucky in this. I am just saying this is their take on BACT.

MS. THOMPSON: I hope I am correct on this and Mr. Gregory can correct me.

Spurlock Four did not go through the MACT process.

Spurlock Three did go through MACT because it predated the camera rule.

And the ACl limit that was included in Spurlock Three is equivalent to the same HCl limit that is up there for Spurlock Four.

MR. BUCKHEIT: So the 0035 is a MACT limit that apparently is being complied with?

MR. DOWD: Spurlock Three.

MR. BUCKHEIT: Spurlock Three has been permitted and constructed and operated at 0035.

MR. DOWD: Right.

MR. BUCKHEIT: So why is that not the floor.

MR. GREGORY: Actually, Spurlock Three is not meeting the mercury limit anywhere near --

MR. BUCKHEIT: With the MACT permit, I don't think you get to make that argument.

MR. DOWD: We traded off between hydrogen

chloride and mercury. It was that simple.

MR. GREGORY: The real crux of the issue is that the chlorine oxidizes mercury.

It basically forms a mercury species that is more easily removed by the treatment.

MR. BUCKHEIT: And I agree with that and I have read that and I accept it.

As we go through the MACT floors, the best controlled similar source, you are telling me, we have a source out there that is up and running --

MR. DOWD: But it's not the similar source, Mr. Buckheit.

MR. BUCKHEIT: Why --

MR. DOWD: The similar source is Seward.

MR. BUCKHEIT: No, no.

MR. DOWD: Because you go to a similar performing similar source.

Well, you know, the cases disagree with you on that one.

MR. BUCKHEIT: The similar --

MR. DOWD: It can be one source and that's what we looked at. We looked at Seward as the best performing similar source.

MR. BUCKHEIT: You are saying that the

Seward CFB is the only CFB that you have to look at?

MR. DOWD: We're saying --

MR. BUCKHEIT: I am willing to go with you and not look at PC and SCPCs and the rest of it, but the similar source category, I think we all agree is the CFB category.

MR. DOWD: And we did look at that. We looked at that. There is a big tradeoff between hydrogen chloride and mercury.

MR. BUCKHEIT: First of all, Bill Maxwell's single slide doesn't tell me whether this plant can meet both these limits at the same time.

However, we have a MACT floor obligation for each of those four things to comply with.

I don't know that the law lets us say: Well, we have a tradeoff, that we are not going to meet one MACT floor, because we think we need to do that to meet the other MACT floor.

MR. DOWD: Well, then you are really in a conundrum, aren't you?

MR. BUCKHEIT: Well, it's how are you going to meet it?

It's true if you can't meet it.

MR. DOWD: I mean, this is the conundrum we found ourselves in.

MR. LANGFORD: Mr. Dowd, or Ms. Thompson, you briefly mentioned some cases.

Is there any established precedent on the use of more than one similar source for individual HAPs?

MS. THOMPSON: No, sir. There is not. And because we were confused about this issue I called EPA to find out which is the correct way to do it.

I actually did speak to Bill Maxwell.

I said: Do we take an approach where we take the lowest number for each plant we can find, and do that, or do we take a more realistic review where, because there is an interaction between pollutants, we take that into consideration.

His response was: I don't know, because we are further under litigation, so either way is correct and either way is wrong.

We chose to take the more realistic approach and acknowledge that there is a reaction between the chemicals, and that is why we stuck with one plant.

MR. BUCKHEIT: Here's my problem -- looking at the -- again, very good acid gas control system, and the fact that the acid gas is being controlled, inside the vessel.

You are going to be at low chlorine levels regardless -- in the vessels -- regardless of what your regulations says.

See, we are not changing here in this whole discussion, what the pollution control device is and what the engineering is.

We are only looking at what's the right number.

So if the chlorine is going to get wiped out in the CFB, and you can't meet the mercury level, that is going to happen whether or not -- we can't change that by writing a permit.

MS. THOMPSON: That's correct.

MR. BUCKHEIT: So what we can do is create a risk that this permit gets shot down in litigation, and the plant gets held up for years if we don't select a MACT floor that represents the performance of the best performing similar unit.

And one of my goals and why I voted to take this permit -- if I was interested in

having this plant not built, I would have said: Don't take the permit.

Because, in my view, the way the permit -- the shape the permit was in in March, there was a very high likelihood it would have been overturned.

And so I am looking at this whole permitting process with a legally defensible, environmentally protected permit that allows this process to go forward, this project to go forward.

I feel a real risk here, if we don't set the MACT floor at the level of the best performing similar source. And again it can't change the internal engineering.

MS. THOMPSON: Yes, sir, I agree with that.

I will say though, when we did our research to identify sources, we could not find a source that had both a low HCl number and a low mercury number.

And as we stated earlier, we felt like mercury was the greatest concern.

So we did a number -- a reasonable number what we thought was a very reasonable number --

THE REPORTER: Wait. Stop, stop, I'm having a --

MR. BUCKHEIT: Breakdown?

(Whereupon, there was a discussion held off the record while the reporter adjusted her machine.)

MR. LANGFORD: Let me try to get to a point.

I think the purpose here is to have the department express their positions, and we question them so that we understand their positions and then we begin advocating other positions.

MR. BUCKHEIT: Well, we are not going to have a further opportunity.

Bear with me.

The issue is compounded, because we also have C0 and PM. And it's going to be virtually impossible to have a single unit for each of them. And if you look at 188 different HAP pollutants, you are never going to find a unit that has been stack tested for all of them that you're going to say is the lowest best -- I am not -- I'm really not saying you're unreasonable here.

I am saying there could be a problem.

MR. LANGFORD: And I think the -- what we choose to do with that later -- I think we have heard from staff as to what their considerations were and how they have established it, and so I think that part of the information is in the record and Mr. Paylor -- would you like to say something?

MR. PAYLOR: I would like to say that, I appreciate and applaud the board's effort to get us to the best possible permit.

Our staff knows the work that they're doing. They have done it for a long time and I do not accept the premise the previous permit was ripe for overturning.

MR. LANGFORD: We will just note that without getting into a discussion over it.

What is your next item there?

MR. DOWD: The next item would be hydrogen fluoride.

Hydrogen fluoride is controlled by limestone injection. The Wise County project's hydrogen fluoride limit is .00047 pounds per million BTU on a three-hour average.

I think it's important to note that

Seward -- the best performing similar source, has no HF number.

However, our number -- the number in the Wise County permit appears as stringent as any other operating CFB.

And I put the Mid Atlantic Energy and AES Puerto Rico, both of which are pulverized coal units, down there as an example of the closest HF limits that we could find and they are still --

MR. BUCKHEIT: I think you mean CFB.

MR. DOWD: No -- I believe -- AES is a CFB. That's correct.

Mid Atlantic is at PC -- that's a pulverized coal.

So our limits are more stringent than they are.

MR. LANGFORD: Okay. Moving along.

MR. BUCKHEIT: Mike, do you have HF performance data that you looked at?

MR. DOWD: No. I didn't have it.

Turning to the HAP metals -- we used PM as a surrogate for the HAP metals because EPA uses PM as a surrogate for the HAP metals.

We believe we followed the approach set

up by the cases especially the Copper Smelter case, which used a three-part test to determine when you could use PM as a surrogate for the metal HAPs, and we believe we met that test here and we don't have to go into it.

Metal HAPs are controlled by fabric, filters, which we have here. I think it is important to note that we are requiring in the initial stack test for the project, stack tests for those following HAP metals.

MS. THOMSON: For a point of clarification --

MR. DOWD: Yes.

MS. THOMSON: EPA uses PM as a surrogate for metal HAPs -- do you mean in setting MACT standards?

MR. DOWD: Yes, it does. Yes.

MS. THOMSON: Okay. Not just in -- okay.

And just to reinforce this because I was a little confused. I believe one of the sets of comments from NRDC asserted, if I remember correctly, that we had to set different emission limits for these and the other -- there are actually many HAPs emitted from coal fired facilities under Section 112-G.

And obviously, as DEQ has a different approach there, and you're citing EPA as a precedent, so could you elaborate on that?

MR. DOWD: Yes. We believe that the case law fully supports what we are doing here.

In the National Lime case, which is really the seminal case on this, they set forth a three-part test for when you use PM, for when EPA can use PM by analogy is stated as well -- use PM as a surrogate for HAPs.

And the test -- the three parts are as follows: First, that the HAP metals are invariably present in the particulate matter.

And that is the case here. All these metals are in the coal combustion -- they are a product of coal combustion.

The second prong is that PM control technology indiscriminately captures HAP metals, along with other particulates.

And we believe that is true here as well.

The fabric filter takes in particulates regardless of what type they are. They capture the carbon particulates equally well with the metal HAP particulates.

And the third prong of the test is that

PM control is the only means by which facilities achieve reductions in HAP metal emission.

And we believe that to be the case.

It is the state of the art for controlled metal HAPs.

So we believe that, you know, following EPA's approach as supported by the D.C. Circuit Court of Appeals that this is the proper way to go, and that it protects human health and the environment to the maximum extent possible, with respect to these metal HAPS.

MS. THOMSON: So those -- if in fact you were issued a permit and used PM as a co-control and were sued on that point, these are the case law precedents, and also the EPA's recomendations and past practices plus the no known greater efficiency, that is fabric filter, and those technological legal and policy precedent that you would use to buttress that decision?

MR. DOWD: Yes, Ms. Thomson. We believe we are on very solid ground with that, and we believe there is no better way to protect --

MR. BUCKHEIT: I totally agree with that.

MR. DOWD: Thank you.
MS. THOMSON: Thank you.
MR. DOWD: Okay. Now, having said all that, we believe that the PM limit is as stringent as any we have identified especially for CFBs.
Our limit -- the limit of the Wise County project is .010 pounds per million BTU on a three-hour basis.
Compare that to another CFB -- JEA Northside -- that is down in Jacksonville. They are at .011 pounds per million BTU in a three-hour average.
We also have a 30-day rolling average in ours -- .009. JEA Northside has none.
Another example, Spurlock Four which has been permitted -- we have the same 30-day rolling average, .009 limit that they have and Spurlock Four does not have a three-hour limit.
So we believe our PM limit is as stringent as any out there.
Turning to VOCs as a surrogate for -- we use that as a surrogate for organic HAPs -- again, because EPA uses VOCs as a surrogate for organic HAPs.

MR. BUCKHEIT: Did EPA use VOCs -- I know they did not use it in the boiler MACT. What about the BTU MACT?

For coal combustion, I thought C0 was the surrogate of choice.

MR. DOWD: Well, we looked at both.

I mean, we looked at VOC as well.

MR. BUCKHEIT: Well, are both coming in the presentation?

MR. DOWD: Yes.

MR. BUCKHEIT: If it is belts and suspenders, there is no problem, but if it is either/or --

MR. DOWD: Oh, no, no, no. We use both. We are saving CO for last.

MR. BUCKHEIT: Okay.

MR. DOWD: EPA uses VOCs as a surrogate. Again the control for VOC is basically good combustion practices.

There is no other cost effective methods for controlling VOCs, especially from a power plant.

And I just wanted to note here that VOCs are anticipated to be higher when burning biomass.

Now, I am not saying that you take that into account, setting the MACT floor. I just note that if the VOC number is lowered, it may restrict the plant's ability to burn biomass to some extent.

MS. THOMSON: I'm sorry.

MR. DOWD: Yes.

MS. THOMSON: If it is lower than what it is here, it may restrict -- you said --

MR. DOWD: To some extent, yes. Yes.

I don't know what that quantification would be. Generally, the more biomass you burn, the more VOCs are emitted, regardless of your combustion control practices.

MS. THOMSON: I think what I hear you saying is you don't anticipate that that will be a restriction of this VOC standard?

MR. DOWD: We don't know. The VOC standard goes down -- if indeed, it is lowered from what it is in this permit, it may or may not restrict the project's future ability to burn biomass, because it may not be able to meet the limit. But we can't quantify it.

MR. BUCKHEIT: But you have -- you said generally its good combustion practices.

MR. DOWD: Yes.
MR. BUCKHEIT: And that's true, but we have an oxidation catalyst and we have after burners.
MR. DOWD: Biomass contains more natural VOCs than coal does, is my understanding.
MR. BUCKHEIT: All I'm saying is there are other control techniques beyond good combustion practices.
I'm not saying you need to get there, but there are such thing as oxidation catalysts and after burners.
MR. MOORE: Mr. Dowd.
MR. DOWD: Yes.
MR. MOORE: I think I heard you say at the limit that you are setting here, it should not interfere with any biomass that the company might want to use, and if that is up to their design limit of 20 percent?
MR. DOWD: I don't know.
MR. FEAGINS: I believe that's correct.
MR. DOWD: Staff tells me that's correct.
MR. MOORE: That is correct.
So it should not interfere with any biomass that's designed to burn up to

20 percent.

MR. DOWD: Yes, Mr. Moore.

MR. BUCKHEIT: Are there -- within the 59 or 60 HAPs that are expected to come out of coal combustion, are there any organics that are not considered volatile, that wouldn't be picked up?

MR. DOWD: Not to our knowledge.

VOC limit in the permit instead of .005 pounds per million BTU, Seward's limit is the same.

The Robinson permit actually has a slightly higher VOC limit. I think the important thing here is that the limit here is as stringent as any operating CFBs, the AES Puerto Rico and Mid Atlantic is of course --

MR. BUCKHEIT: Okay.

MR. LANGFORD: Just note it and we'll move on.

MR. BUCKHEIT: No, no. What is the limit for AES Puerto Rico?

I mean, if we're going to not do a MACT floor --

MR. MOORE: AES Puerto Rico is operating. It has been.

MR. DOWD: Yes, it is.
MR. MOORE: I mean, for a good while.
MR. DOWD: It has been. It was discussed at length earlier.
MR. MOORE: And what is their limit?
MR. DOWD: My folks are digging that up.
MS. McCLEOD: I believe that it is .0047 pounds per million BTU on a three-hour average.
MS. THOMSON: .0047 pounds per million BTU per three hour?
MR. BUCKHEIT: Explain to me why, if you wouldn't do .0047, match it and be done.
MR. DOWD: That is the number that folks came up with.
MR. BUCKHEIT: Okay.
MR. LANGFORD: It is noted that AES has a slightly lower limit, and we will revisit that after the lunch hour.
MR. DOWD: Okay. And finally, carbon monoxide.
DEQ uses carbon monoxide, CO, as a surrogate for organic HAPs, as I said before, EPA uses CO as a surrogate for organic HAPS also.
The control for carbon monoxide is good

combustion practices, and there really is no other control technology that is identified to control carbon monoxide on a CFB --

MR. BUCKHEIT: Again, I have to raise the possibility of oxidation catalysts and after burners. I don't think oxidation catalysts should be considered because we are looking at C0, not for C0's sake, but as a surrogate for HAPs, so you wouldn't consider an oxidation catalyst unless it also reduced the HAP.

If the catalyst is specific to C0 then it wouldn't be any good.

I don't know the answer to that question.

MR. DOWD: Of course, that would be a beyond-the-floor MACT measure because no CFB --

MR. BUCKHEIT: I am looking at your bullet. That is all I am responding to.

MR. DOWD: Rob.

MR. FEAGINS: Rob Feagins.

The theoretical possibility of after burners -- you are absolutely correct. They were discounted in the BACT analysis.

MR. BUCKHEIT: They were probably too expensive to BACT. And they are probably not there for the MACT floor.

I am just saying that is not an accurate statement.

MR. DOWD: Well, when you take into account the requirements of the law, we believe it is an accurate statement because of the cost effectiveness.

Now, we get into the weeds on this, but we are almost set to wrap here.

There is a relationship between carbon monoxide and NOx, and also like the VOC, CO is anticipated to be higher when burning biomass.

The Wise County C0 limit of .15 pounds per million BTU on a 30-day average appears as stringent as any operating CFB, except for AES Puerto Rico, and Seward, actually, is .15 pounds per million BTU on a three-hour basis.

They have lower limits -- lower C0 limits.

They also have higher NOx limits.

We did not propose to lower the C0 limit here because the Wise County project has lower NOx limits than either of those two other plants, and we did do not want to jeopardize the permit's NOx limit by decreasing the CO limit.

And finally, I just want to note that neither AES Puerto Rico nor Seward is permitted to burn biomass.

MR. BUCKHEIT: Do you have an emissions data for AES Puerto Rico or Seward?

I mean, I'll just have to note for the record that with current generation NOx controls even as NCR, the C0 NOx tradeoff that people were worried about 15 years ago has largely been addressed.

MR. FEAGINS: We do have some performance test data for the Spurlock Number Three, and their limit, as is indicated there, I believe -- no, I didn't have it there.

MR. BUCKHEIT: I am looking at AES Puerto Rico and Seward.

MR. FEAGINS: Okay. I don't have the data. Okay.

Okay. We have the data for AES Puerto Rico. It shows carbon monoxide -- an average -- this was taken in November of 2007 -- 0.047, and that is pounds per million BTUs.

MR. BUCKHEIT: So they are about half your number.

MR. FEAGINS: Less than half our numbers.

MR. MOORE: Quite a bit less than half.
MR. LANGFORD: Get to the summary.
MR. DOWD: In summary, the Seward plant was determined to be the best controlled similar source, on the basis of its control technology it employed and on its mercury emission rates in their stack test.
The mercury limit was based on the Seward stack test, adjusting for stack test accuracy at low levels. This is the only -- the Wise County project is the only CFB required to install activated carbon injection, and it represents the beyond-the-floor MACT measure.
And the other HAP limits are as low or comparable to Seward, and the other identified sources.
And that concludes the presentation.
Are there questions?
MR. LANGFORD: Are there questions of general interest or a general part that haven't been asked already?
MR. BUCKHEIT: I'm questioned out.
MR. LANGFORD: We've got one that is questioned out.
I believe, Mr. Dowd, your staff will be

available after lunch, if additional questions come up during deliberations on these topics.

MR. DOWD: We're not going anywhere. We will be here.

MR. LANGFORD: It's 12:40 and on the schedule Dominion is going to take another hour.

MR. MOORE: I certainly am not going to have much, so when Mr. Hanson gets on, we're ready to go.

MR. LANGFORD: We will be when we get back, because we will still have 45 minutes when we get back.

Otherwise we are going to be pressing for people -- the public to leave and go get something to eat and come back. We need to do this now.

Cindy, do you have any words of guidance for us?

MS. BERNDT: This is no lunch here. That might help you.

MR. MOORE: I move, if it is not out of order that that we proceed at this time.

MR. BUCKHEIT: Well, without lunch, let's go.

MR. LANGFORD: If there is no lunch, I guess we're going to go.

(Whereupon there was a discussion held off the record.)

MS. HARDY: Mr. Chairman, members of the Air Board, Mr. Paylor, Mr. Josephson, thank you for the opportunity to be here today.

In the interests of time, I am going to dispense with my presentation and ask that Pamela Faggert, our chief environmental officer, come forward because I only had one slide, and she has a series of slides.

You can look at the slide very quickly. The proposed facility that we're here about today is part of a four-pronged effort to combine conservation, renewable energy, and traditional generation, both coal and nuclear for baseload and gas for intermediate, to meet Virginia's growing needs.

We are the fastest growing state in terms of electricity in the 13-state mid Atlantic region.

So against that backdrop we have tried to put together the very best possible project for this particular site here in Wise County.

I would like to thank DEQ, and all the staff at DEQ who are here today, because along with you, as members of the board, they have spent hundreds and hundreds and hundreds of hours working on this permit application, and, you know, getting information from us, and hopefully giving you the information that you wanted and needed, in order to make a decision today.

Thank you very much, and now I'm going to turn it over to Pam Faggert, our chief environmental officer.

THE REPORTER: Ma'am, I'm sorry. Could you repeat your name for me?

MS. HARDY: My name is Eva T. Hardy, executive vice president of Dominion Resources.

MR. LANGFORD: Ms. Faggert, before you start, could we get copies of your presentation for us to mark up and follow along.

MS. FAGGERT: Yes, sir.

Thank you, and good afternoon.

My name is Pam Faggert. I am vice president and chief environmental officer for Dominion.

This slide shows a permitting process

since our first submission to DEQ on this project nearly three years ago.

As you know, we presented information to you on the project at your November, January, and March board meetings.

And we are pleased that the revised draft permits are before the board today for your consideration.

As Eva mentioned, since the board's last meeting, we responded to your questions with hundreds of pages of documents in support of our permit application, and I would like to present some summary information to you now.

The draft permits require a full suite of emissions controls. It is important to understand the facility will operate as a system, where all processes must be integrated and optimized to insure compliance with each of the emission limits.

And yes, there are some tradeoffs.

The proposed air permit requires BACT and MACT and are extremely restrictive.

The facility will be fitted with the latest in emission control technologies for sulfur dioxide, nitrogen oxide, particulates,

mercury, and the other pollutants.

S02 emission controls will be installed include limestone injection in the boiler, the scrubber. NOx controls include low NOx temperature combustion and SNCR. Particulate controls include the fabric filter baghouse, SNCR, and the scrubber, and of course now the permit requires activated carbon injection for mercury control.

As you can see on this table the proposed permit limits emissions to significantly lower levels than the new source performance standard requires.

In all cases, the Virginia City project limits meet BACT or for the HAPS, MACT.

The revised permit limits do reflect the reduction in emission levels, and also reflect a requirement that we install activated carbon injection.

As you also know, the most recent draft requires lower S02 emissions and also a lower coal sulfur content.

With regard to the MACT permit, as shown in our MACT application, we have proposed to install a full suite of controls which

constitute MACT.

Mercury control is inherent to CFB technology. It is controlled by the flue gas scrubber, the baghouse and the activated carbon injection.

This facility will become one of the first CFBs in the world to have ACI installed.

Prior to the court decision vacating EPA's mercury rule, the draft PSD permit had set a mercury limit of 72 pounds per year.

When we had that proposed limit, we did deposition analysis, which showed that there would be no significant impact to the Clinch River watershed, based on the 72 pounds per year.

And of course, as you know, the original MACT permit set a lower limit of 49 pounds per year.

And the draft permit before you today, has an extremely stringent limit of 8.19 pounds per year, based on a pound per megawatt hour rate, which is the strictest in the nation for all similar CFB boilers.

We do not believe that either the 8.19 pounds per year or any lower limit have been

demonstrated to be achievable in practice at similar facilities using the monitoring technique that we will be required to employ at Virginia City.

With that said, we will operate the air pollution control equipment, which we do believe is the best ever installed anywhere, to the very best of our ability to demonstrate the best emissions that can actually be achieved in practice.

With regard to the other HAPs, we will install a full suite of controls to control HAPS.

The acid gases will be controlled with limestone injection in the boiler, and the scrubber. The organics will be controlled by good combustion practices and we believe that the ACI may help for some of them.

The inorganics will be controlled with a fabric filter.

We have modeled the HAPs emissions and found that all of them are less than three percent of Virginia's annual significant ambient air concentration standard.

This is well within the allowable limits.

In addition to this permit, as part of our plan, we are proposing to convert our Bremo power station, in Fluvanna County, Virginia from coal to natural gas.

Bremo does not have the state-of-the-art emission controls that the Virginia City facility has.

The conversion is possible while still allowing the company to meet the demands of our customers, because of the base load capacity which will be provided by the Virginia City project.

We would not be able to serve our customers' baseload energy needs and convert the Bremo from coal to natural gas without the additional baseload capacity provided by the Virginia City project.

The conversion of Bremo will result in a large net reduction of emissions of sulfur dioxide, nitrogen oxide and mercury after the Virginia City facility is operating at its full capacity, even assuming that the newly converted gas units of Bremo operate 100 percent of the time, which is unlikely and would be a significant departure from utility

practice for gas-fired units.

Again, the net S02 reductions with Virginia City operating at its permitted limit and Bremo operating at 100 percent capacity after it is converted from coal to gas are net S02 reduction of 9,967 tons per year, a net NOx reduction of 926 tons per year and a net mercury reduction of at least 115 pounds per year, based on historical emissions from Bremo power station.

Additionally, the conversion at Bremo will reduce C02 emissions from Bremo by at least 300,000 tons per year, and probably significantly more.

MS. THOMSON: I am sorry. I am just staring at the response that you sent to me about the conversion -- and this was back in April, in which you estimated -- I think I am reading this chart correctly -- the C02 emissions at Bremo at 1.3 million.

So you revised that?

MS. FAGGERT: No, no. You are correct. Those are the current actual C02 emissions from Bremo.

And I'm being very conservative to say

that conversion from coal to gas --

MS. THOMSON: How much it will net?

MS. FAGGERT: Will net 300,000.

I believe the actual net will be much larger at Bremo, because the 300,000 is assuming we operate at 100 percent of the time on natural gas.

That is highly unlikely that that will happen. We will probably eliminate most of the C02 emissions from Bremo, but conservatively, at least 300,000 tons per year.

MS. THOMSON: Well be reduced by the conversion?

MS. FAGGERT: We are at 1.3 now. We will be at one in the future or less.

MS. THOMSON: Okay. Thank you.

MS. FAGGERT: You are welcome.

A summary of the revised draft permits, mercury emission limit has been reduced from the previously draft by 89 percent to 8.19 pounds per unit -- a very strict limit.

S02 emissions have been reduced by more than 800 tons since the previous draft permit to 2,400 tons per year.

Additionally, Dominion and the Forest

Service and DEQ reached an agreement in December, which is contained in the permit, that the Virginia City hybrid energy center will protect sensitive Class One areas, the federal agreement protects all Class One areas surrounding the Wise County project, including the Linville Gorge Wilderness area.

Dominion will limit or otherwise mitigate the station's annual S02 emissions so that the net total is no more than half of the current permitted limit.

It used to be half of the higher limit, now it is half of the lower annual S02 limit.

THE REPORTER: I am going to have to stop the proceedings again. I am so sorry.

(Whereupon, there was a discussion held off the record while the reporter adjusted her machine.)

MS. FAGGERT: Additionally, by 2015, sulfur dioxide emissions in the region will decrease by over 5,800 tons, considering the operation of the Virginia City facility at full capacity and the emissions reductions that will be made at AEP.

So there will be net S02 emissions

reduction in the vicinity of the Virginia City facility.

This does not include a reduction from Bremo, which I have already mentioned will alone result in a statewide net reduction of SO2 emissions, NOx emissions and mercury emissions.

The nearly three year permit process has resulted in revised draft permits which meet, and in most cases go well beyond all Clean Air Act requirements, which are designed to protect human health and the environment.

In view of the need for this project's baseload energy, the stringency of the draft permit, and the cost of additional delays to our rate payers, we respectfully request that the air board approve both permits today.

Thank you for the opportunity to speak, and I would be happy to take your questions now.

MR. MOORE: This plant is presented as one of -- as a hybrid in that it has 20 percent -- it is designed to take 20 percent biomass, but I understand from the staff -- if I were to ask you, can we write in the permit that it

will do 20 percent biomass every year, your answer would be you wouldn't like that.

And can you tell me -- you know, how much will it run per year that we can count on?

MS. FAGGERT: I think that number will vary from year to year. I would anticipate -- and I am going to turn around and check with my experts, but I believe the answer is between 5 and 10 percent.

They are nodding their heads.

MR. MOORE: Let me ask them to nod, and ask two questions.

Number one, how much will it do -- let's say 10 percent -- if it is put into the permit that, at least 10 percent of the heat input for the plant will be from biomass each year.

The second question -- that's question one.

The second question is: Well, we don't know whether it will do quite 10 percent every year, but when you're considering emissions limits you can consider 10 percent. It won't have to be 10 percent, but if you don't do that, you know, it will cover S02 emissions or whatever it is some other way.

MS. FAGGERT: The answer to the first part of your question is, if you're asking what our preference would be, it would be rather that you limit the number of hours per year that we could combust coal, giving us the option to not combust coal or to combust biomass, rather than setting a fixed biomass restriction.

MR. MOORE: You know, if I could say -- if we just took 10 percent -- and I don't have the number -- if we would say 10 percent, we would just say that you cannot combust coal more than 90 percent of the time.

MS. FAGGERT: We prefer it be structured in terms of a BTU per year basis.

MR. MOORE: Okay. All right.

MR. BUCKHEIT: Let me try --

MR. MOORE: Okay. Let me -- okay. That is the first question.

The second issue -- you know, how much can we count on when we look at, you know, emission limits?

MS. FAGGERT: If I could kind of back up to the second half of your first question, there is biomass in Virginia now.

However five to ten percent of the total heating value for this project would be a large amount of biomass megawatts, compared to the current biomass market in Virginia.

MR. MOORE: And we understand that and everybody wants still to have some trees in Wise County.

MS. FAGGERT: Right. We are not proposing to burn anything other than waste biomass. We are not proposing to cut any trees.

MR. MOORE: I understand.

MS. FAGGERT: So, back to your original question, it would be something that you would want to develop for the market.

In other words, I wouldn't want to say: Oh, we would anticipate burning, say 10 percent the first year.

I would imagine that we would work into the biomass market, 5 percent, 6 percent, 7 percent, 8.

In other words, in the long run, we might be able to burn more biomass.

In the near term, probably less, because the market is a market we do hope to develop.

MR. MOORE: So you're relatively comfortable with 5 percent. You think ultimately we could get to 10, but you would rather have that as a limit, to the extent that there is a limit, on the heat input from coal?

MS. FAGGERT: Yes. If 90 percent of the maximum possible combustion hours could be coal and then five to ten percent --

MR. MOORE: Not combustion hours -- combustion heat content.

MS. FAGGERT: Oh, we were thinking combustion hours, because the maximum amount of time you could operate --

MR. MOORE: No, I said that, and you said you would rather have it -- that you would -- you would rather have it stated in BTUs.

MS. FAGGERT: Yes. BTUs per year. Right.

MR. MOORE: Okay. That's -- okay -- we're saying the same thing.

MS. FAGGERT: I hope so.

MR. MOORE: Well, it is BTUs per year. You won't have -- the coal will not -- will not produce more than whatever it is. It's -- what is it? It is a six million two hundred and

sixty four million BTUs an hour times --
MS. FAGGERT: 8,760.
MR. MOORE: 8,760 times .9.
MS. FAGGERT: Yes. We came up with 27,436,320 times ten to the six.
MR. MOORE: I just did that. But the numbers that I laid out would be the right way to make the calculation.
MS. FAGGERT: Yes. As a maximum fossil BTUs per year, 90 percent of that could be coal and up to 10 percent of that could be biomass -- not from behind, yes.
MR. MOORE: Give me that number again so I don't have to do the math and spout it.
MS. FAGGERT: Okay. 27,436,320 times ten to the six BTU per year.
MR. MOORE: And the way you have got there was the way I indicated -- you took the hourly heat content times 8760 times .9.
MS. FAGGERT: Yes. Mark Mithcell is going to add some value here.
MR. MITCHELL: I'm Mark Mitchell.
I'm the director of fossil and hydro projects.
I just checked that number. It is based

on the BTU value. We agree with you. But we are going to check our numbers to make sure we have got the right numbers for you.

MR. BUCKHEIT: Let me try to --

MS. FAGGERT: That number was at 100 percent. There would be 90.

We are going to check and get back to you. You know what -- we are going to check and get back to you.

And again, if there were going to be a requirement, we would request that it would be phased in -- 5 percent -- to develop the market.

MR. BUCKHEIT: And on that, I think we are on exactly the same wavelength.

I was sort of thinking that we might be able to have this conversation here where we could come to an agreement on a feasible starting point and a feasible rate of incremental growth in the market.

I mean this project was sold to the legislature and the governor to have a Virginia energy plan in Wise.

I think it is an important step forward for C02 is in actually developing a CO2 base.

I was concerned that the original draft permit -- I mean, there are a lot of cars out there that are fossil fuel capable, and they always run out of gas.

Do -- I think I hear you saying that you would be amenable to a percentage of your actual -- your operating days in a year would be renewable based -- or is it just a cap on the number of hours a year that you run coal?

I mean, we know that you're not going to run more than 90 percent of capacity factor anyhow, and I don't want to get into later generation. If we need generation we need generation.

How does that concept strike you, that we develop a percentage that we -- back before here we were talking about that would be feasible to start with, and then have it grow -- I was thinking something like 5 percent when you start up, and then grow a percent a year for five years then be done, so it would never go above ten.

MS. FAGGERT: I would want to chat with my colleagues a second about that.

Again our preference would be a

restriction on the amount of coal in the event that biomass is available in any particular given year.

MR. MOORE: Well, maybe a biomass out if it's not available, or that kind of thing.

MS. FAGGERT: I think you understand our concerns.

MR. MOORE: Yeah.

MS. FAGGERT: In any given year, if the biomass isn't available, what do we do -- ten percent of nothing, you know --

MR. MOORE: No one wants you going in and cutting down trees in our national parks.

MS. FAGGERT: Nobody wants that.

MR. MOORE: And you don't want that.

MS. FAGGERT: Yes.

MR. MOORE: And so let's see if we can maybe you-all can huddle and come back after some break or something.

MS. FAGGERT: That sounds like a good idea.

MR. MOORE: I would like to try to figure out some way to reach an agreeable position with you-all where we can put into a permit some mechanism to have this plant truly be a

step towards, you know, addressing the carbon issue.

MR. MOORE: We don't want it so bad. You have the out of just don't burn it -- unless it is not available. So a percentage of the heat input that actually goes in, and ramp it out. I think that sounds good, with an out -- if the biomass is not reasonably available or whatever words -- I am sure you have got a lot of words in there.

MS. FAGGERT: We do. We would appreciate the opportunity to word it.

MS. THOMSON: Just so -- when we continue this discussion later, I'm sort of thinking about a baseline of control of emissions of carbon dioxide, which I know you have estimated from the facility, about 5.3 million.

Is that number still holding?

MS. FAGGERT: Yes. That's correct.

MS. THOMSON: So in other words, if we were to work out some kind of limit on the -- either biomass use or non-use of coal, then we would reduce the baseline carbon dioxide emissions by that percent.

Is that correct?

MR. BUCKHEIT: The fossil carbon emissions.

MS. FAGGERT: That is, in fact what would happen.

MS. THOMSON: So I guess what I would like to be able to get -- and we don't have to do this now -- is an estimate of at different -- under these different kinds of proposals, how much carbon dioxide emission reduction.

So I would just like to have an agreement on that.

MR. BUCKHEIT: But wouldn't it be just a percentage of biomass of the carbon --

MS. THOMSON: I think so. Yeah.

MR. LANGFORD: It has to be organic. It has got carbon in it.

MR. BUCKHEIT: But is fossil CO2

MR. LANGFORD: I didn't realize there was a different kind of C02.

MR. MOORE: Well, we will let you read about that.

MR. LANGFORD: As a chemist, carbon dioxide is a single --

MS. THOMSON: Do we have any more questions for Dominion?

MR. LANGFORD: No.
MS. FAGGERT: Thank you very much.
MS. THOMSON: Thank you.
MR. LANGFORD: Ma'am, I assume you guys will be around after lunch as well, if by chance there are additional questions that might be raised.
MS. FAGGERT: Absolutely we will be here.
MR. LANGFORD: Cindy, where's lunch?
MS. BERNDT: En route. I just called. They said somewhere between ten and fifteen minutes.
I am going to propose that we go ahead and break, and then given the uncertainty of our lunch, do you just want to plan on 2:30?
MS. FAGGERT: Yes. That works for me.
MR. LANGFORD: It's already after one. And 2:30 will give us enough time to make sure that everyone gets down and back.
All right. We'll adjourn for lunch and then we'll come back at 2:30.
(Whereupon, a lunch recess was taken.)
MR. LANGFORD: I'll call this meeting of the State Air Pollution Control Board back to order after the lunch break.

And one of the first things -- we have got a couple of housekeeping things to do first. I want to again check to see that we do have an audio feed from the fifth board member, Mr. John Hanson, and he is going to be on the speaker phone.

And John, do you hear us all right?

MR. HANSON: Yes, I can, Richard.

MR. LANGFORD: And I think -- you guys heard John?

MR. BUCKHEIT: Yup.

MR. LANGFORD: It looks like the technology is working, John.

Thank you very much.

The second thing that we're going to do, is -- this has been a long process, and there may have been opportunities for individual board members to have had communication with one side or the other outside of the normal comment periods.

And so this is an opportunity for any board members who have had those kinds of comments to be able to disclose them publicly before we begin deliberations.

And these are called "ex parte

communications."

Does anyone wish to make a disclosure?

MS. THOMSON: Over the past many months, I have conversed and many times been approached about this issue by -- for example, by individuals. I have had conversations with various government employees -- for example, the National Park Service, academics, and representatives of environmental groups and businesses.

All the information considered in my decision is in the voluminous record.

MR. BUCKHEIT: I have also been called by members of the media, state representatives, members of the public, about my deliberations -- not about the rules -- about the issue.

These folks just want to know about the status, what the scheduling might be, and I responded to those requests.

If you looked at my April 14th letter, 26 pages, single space -- research -- obviously, I spent a lot of time looking into this. This process has evolved over the informal inquiry, the formal fact gathering.

I have had no substantive communications

with any party in this matter.

MR. MOORE: I have had no substantive communication with any party at any time.

MR. LANGFORD: And I haven't had any substantive communications with parties from either side.

Obviously, we have had individual discussions with DEQ staff and been briefed there, but not by other parties.

John, did you have anything you wanted to say?

MR. HANSON: I have had no substantive communications.

MR. LANGFORD: Okay. Thank you.

I believe Dominion had some homework they were doing during the lunch break, and I'll give Pam Faggert a moment to report on those results.

MS. FAGGERT: Yes, sir.

In fact, I would like to hand it out, if it is okay -- but I would first like to start -- we believe we have crafted a condition with regard to biomass that meets the intent of what Mr. Buckheit and Mr. Moore were asking about. And I'll hand that out in a minute.

But I would like to say that we crafted this condition in the context of the current draft permit.

Everybody knows that the boiler and the controls work as a system, so we offered this in the context of the current draft permit.

If the permit were to change, it is possible that our opinions with regard to this condition would change as well.

MR. LANGFORD: And for John's benefit, when I get this, I will read it, so we will all be able to know what it says.

I'm assuming that you haven't e-mailed it to anybody -- to John or anybody?

MS. FAGGERT: I have not e-mailed it to anybody.

MR. LANGFORD: I didn't think you knew how.

MS. FAGGERT: It was all we could do to print out five copies.

MR. LANGFORD: The document I've been handed is titled "Assumes Current Draft Permit," and then it next says, "Use of Biomass," and it has two numbered provisions, which I assume fit into the current draft

permit.

One of them is labeled "Number 22, Heat Input."

And it reads as follows: After the first 36 months of commercial operation, the company will agree to use at least 5 percent biomass. Starting in the fifth year of commercial operation, the company agrees to increase the use of biomass by an additional 1 percent per year, up to a maximum of 10 percent. For purposes of such biomass requirement, the percent shall be determined by the total biomass heat input for any given year, divided by the total heat input for any given year, averaged over a rolling three years.

And then another -- Provision Number 23: Should market conditions, as evaluated by the company, indicate that biomass fuel has a significant rate payer impact, or promotes tree cutting, such biomass requirement shall be eliminated until market conditions correct.

And that's the text of the document that Dominion has provided to us.

Did you have any questions on that, John, or do you pretty much follow that?

MR. HANSON: No questions.
MR. LANGFORD: Okay.
MR. BUCKHEIT: Ms. Faggert, the one problem with Paragraph 23, that would then give the company sole decision-making process in that.
If we eliminated the "as evaluated by the company," and left the rest of it, so that if it got very expensive or if it was going to promote tree cutting, you have your out clause, but as determined by the DEQ.
I think that might be viewed by others as more of a real commitment rather than your own decision.
MR. HANSON: Hello?
MR. LANGFORD: Yes, John.
MR. HANSON: Hello?
MR. LANGFORD: John?
MS. THOMSON: Somebody else has joined the line, and I don't know who that is.
Somebody picked up the kitchen phone.
MS. FAGGERT: My colleague has a suggestion for that problem.
MR. BUCKHEIT: Sure.
(Whereupon, Mark Mitchell walked up to

the podium.)

MR. LANGFORD: Sure. Could you identify yourself, sir?

MR. MITCHELL: Mark Mitchell, Director of Projects for Dominion.

One thing, I mean, our fuel policy gets reviewed by the State appropriately at the appropriate times, but we would be willing to add in there: Or -- and/or as consulted and approved by DEQ.

MR. BUCKHEIT: It just seems to me like we have --

MR. MITCHELL: We should at least evaluate it, because we --

MR. BUCKHEIT: Oh, yes. You would evaluate it. Your consultant would prepare a report for the board.

MR. MITCHELL: We select a consultant that is agreeable to DEQ and have them do it and we both review the report.

MR. BUCKHEIT: But at the end of the day, if DEQ agrees with you, you get to do it.

MR. MITCHELL: Yes.

MR. BUCKHEIT: Okay.

MR. LANGFORD: Okay. I didn't hear that.

It sounded like you agree to agree?
MR. BUCKHEIT: As I understood it --
THE REPORTER: Mr. Buckheit, would you remove your computer? I can't --
MR. BUCKHEIT: Okay. My bad.
As I understand it, what DEQ is proposing is that --
MR. MITCHELL: Well, DEQ has --
MR. BUCKHEIT: Not DEQ -- Dominion -- Dominion is proposing is that Dominion would retain a consultant who would evaluate the issue, take it to DEQ, and secure DEQ's concurrence.
If DEQ concurs, then everything is, you know, all set.
MR. MITCHELL: Yes.
MR. LANGFORD: Is that correct?
MR. MITCHELL: Yes.
MR. MOORE: Let me ask you this, and this is a small matter, but I think -- you have got "such biomass requirements shall be eliminated."
Can we say "eliminated or reduced"?
Maybe things get bad, but you can still run at two or three percent, and I just don't

want you to feel like: Well, I've got an obligation to get up to six or seven percent, now the market has changed -- you know, we can get some. We could get three, maybe four. But we can't get seven. So we have just got to -- we get to stop.

MR. MITCHELL: How about the and/or -- reduce, and/or eliminate?

MR. BUCKHEIT: As appropriate.

MR. LANGFORD: That's fine.

MR. MOORE: Well, it would be reduced or eliminated. You can't do both.

MR. LANGFORD: Bruce, do you like the language of the first part?

MR. BUCKHEIT: Yeah, I suppose. I mean, obviously -- we will -- the process from here is that we will vote on a permit, with or without amendments, and then DEQ will draft the final language.

I for one -- I think each of the board members will probably want to see it, and I assume that Dominion would want to see it.

MS. THOMSON: Yes, we would like to see it.

MR. BUCKHEIT: So, I think then -- we can

take a crack at it, but people will have a chance to polish it up.

MS. THOMSON: Thank you.

MR. LANGFORD: But, Mr. Buckheit, what we would be talking about would be wordsmithing -- not shortening "yes" to "no" or --

MS. FAGGERT: I would also like to mention again our opinion on the conditions contingent on the remainder of the permit.

MR. MOORE: We understand.

Ms. Faggert, let me ask about a second item, which I think you may be aware of, and that is the idea that if the permittee desires to burn waste coal that you would submit a plan to the board for DEQ, for approval, detailing the pile or piles you propose to burn, and, that the board would have, of course, and DEQ would have the opportunity to approve that plan.

And I would also add that in that the DEQ could -- I am not saying they would have to -- but could have as part of their process, require that when Dominion begins taking coal from a pile, it either removes it and stores it all safely or it burns it all.

I'm not talking about what period of time. It may take 30 years to do that. But it would be permissible for the DEQ to impose a requirement, that if you started working on gob piles, if the right thing to do was finish that gob pile, that could be part of the requirement.

I would also say that as part of that the DEQ, or the board, could not use that process as a way to require you to use more biomass.

MS. FAGGERT: As a point of clarification, perhaps -- and I am not entirely positive I understand exactly all the details of what you're saying -- but our concern -- we would be concerned if there were a requirement to burn any particular gob pile.

As you can imagine, if have you to --

MR. MOORE: No, no. Nobody would know it until you had cut your deal.

MR. BUCKHEIT: Right. That's not where we are going.

MR. MOORE: No, no, no.

MR. BUCKHEIT: What we are looking at is, if the intent of remediating the gob piles is to provide environmental benefit, that benefit

would not seem to occur if you dug up three quarters of a pile and left.

MS. FAGGERT: Specifically, what we -- I think, have agreed to would be as long as the identity of such piles remains confidential business information, the company shall use commercially reasonable efforts to give priority to consume fuels from such coal refuse piles in its fuel limits.

MR. BUCKHEIT: And that I think is fine, that rewrite. Because what we're looking at is we understand -- what we are trying to do is to preserve your ability to maintain low prices, not getting boxed into a corner where you have to make a public announcement of where you're going.

But -- okay -- so that even after you have contracted with a person for the sale of the pile, that you would then -- could then go to DEQ to seek approval of the plan, or, as you put it, you could put it in -- people would have to know where it was in order to be able to evaluate it.

So my thinking is it might be best for you-all to finish your contract, and then put

your proposal in, and then there could be a sort of public evaluation by DEQ, that this is a good one.

But our intent is to not raise your costs and our prices by premature disclosure.

MR. MOORE: Absolutely not.

But at the same time, DEQ would have some input into which piles. I certainly believe and -- that you agree on all that, but it seems to me that if we're going to get into the burning of waste piles, that it is appropriate for DEQ to know ahead of time and to approve which piles, you know, you're going to be burning.

MR. LANGFORD: Let me jump in here and say: I've got two members of my board that are negotiating publicly with Dominion over issues that we have not either previously been briefed on, that are not in the -- that I have seen -- in the response to comments, and I, for one, am not sure I am on board with where they are going in granting an air permit.

What I would like to do, perhaps, is -- I think if we are going to propose this as an amendment to this permit, we need to do this as

a separate --

MR. MOORE: I think we know where you're coming from on that.

MS. FAGGERT: Thank you.

MR. LANGFORD: I believe that we are ready, Mr. Moore, if you wish to have some comment.

MR. MOORE: I would move that the staff BACT and MACT permits, as recommended, be approved with amendments.

I will have some amendments related to S02, and I know that at least two of my colleagues will also have other amendments.

Mr. Chairman, do you want me to just do my amendments?

MR. LANGFORD: Let's deal with this motion first and then we'll start with the amendments.

MR. BUCKHEIT: I -- we have a second also.

MR. LANGFORD: Mr. Burkheit has seconded that motion.

And so we have -- there is a motion on the floor to approve both of the permits, with some amendments yet to be discussed and voted

on.

And we will begin with that process and go through whichever amendments that board members want to offer.

We will vote individually on those amendments, and then whatever the package looks like at the end, there will be a vote then on this particular motion, the way we are looking to move forward.

And Mr. Moore, do you want to start with an amendment?

MR. MOORE: I move to amend the permit as follows:

Paragraph 29, S02 Emissions, change the annual limit from 2469.3 to 603.6.

Change the three-hour limit from .15 to .035 and adjust the pounds per hour for each boiler.

Change the 24-hour limit from .12 to .029 and adjust the pounds per hour for each boiler.

Change the 30-day rolling average from .09 to .022, and add the pounds per megawatt hour on a gross basis.

We would also add the language that we have discussed with respect to the heat content

-- just now, with Ms. Faggert, and I would also -- I put this in, perhaps as a place holder, the following: In the event the permittee desires to burn waste coal, it shall present a plan to the Board for approval detailing the proposed pile or piles to be burned --

MR. LANGFORD: Mr. Moore, may I ask that you put that in a separate motion?

Let's do the sulfur stuff, and then have a separate motion for the gob piles.

MR. MOORE: Right. It is --

MR. LANGFORD: I would like to keep it clear on what we're voting on and not mix them up with two or three things.

MR. MOORE: Okay. The second item then, the Paragraph 41 -- I would delete the provision of air quality related values.

Mr. Chairman, may I speak to that?

That's the National Forest Service communication.

MR. LANGFORD: All right. We have a motion before us for changing sulfur dioxide limits, beginning in Paragraph 29 of the draft PSD permit, and I will trust that the record will reflect the correct limits.

Would you like to repeat those for us again, and then we will seek a second?

MR. MOORE: Yes. Change the annual limit from 2469.3 to 603.6, change the three-hour limit from .15 to .035, and adjust the pounds per hour for each boiler, change the 24-hour limit from .12 to .029, and adjust the pounds per hour for each boiler.

Change the 30-day rolling average from .09 to .022, and add the pounds per megawatt hour on a gross basis.

And then delete Provision 41, Air Quality Related Values.

MR. LANGFORD: All right. We have that motion.

And do we have a second for that motion?

MS. THOMSON: I second.

MR. LANGFORD: Is there a discussion on the motion?

Would you like to make a statement, Mr. Moore?

MR. MOORE: I would like to speak to it.

First, I want to begin by thanking every one who has participated in this process. As Dr. Thomson said this morning, this hasn't been

easy on many of you.

We appreciate your time, your attention and in some cases your courage.

We thank those who have written letters, those who have waited many hours to speak, organizations and localities that have made their presentations and sent us resolutions, analyses and data, the company that has responded to numerous requests from the staff and from the board, and particularly the staff that has collected and provided us with much information and data.

We have read, we have listened, and I believe, while it has been a long process, we are now ready to act.

As we begin, I want to note once more, that we must remember that power plants are not temporary installations. The Wise County facility and its pollution will impact citizens of this Commonwealth for more than half a century. Pollution from the unit could affect the health of generations of our citizens and the environment of our region, including other states, far into the future.

It is the responsibility of this agency

and this board to protect the health of our citizens and the environment of the Commonwealth in considering Dominion's Wise County applications.

The policy of the Commonwealth is first stated in our constitution -- to protect the Commonwealth's atmosphere, lands, and waters from pollution, impairment, or destruction, for the benefit, enjoyment and general welfare of the people of the Commonwealth.

This policy is implemented in the Code of Virginia and our regulations.

You must also remember that this agency and this board are acting as part of and pursuant to our state implementation plan.

Through this step, our actions carry out the Clean Air Act.

It is with this background that we must consider the Dominion Wise County applications and the proposed permits.

I will address S02 limits and have proposed amendments to the staff's latest proposal.

Others on the board, I am sure, will offer other amendments and have comments to

what I have proposed.

The staff proposed permit leaves the three-hour and 24-hour limits as they were in the staff's earlier draft.

The three-hour limit is .15 pounds per million BTU and the 24-hour limit is .12 pounds per million BTUs.

In addition, staff proposed a rolling 30 day average limit of .09 pounds per million BTU.

This 30-day limit has the effect of reducing the annual limit from 3,292 tons per year to 2,469 tons per year.

The staff also proposes that the Forest Service's 50 percent mitigation provision would apply to the new annual limit.

Finally, staff proposes that the 2.28 percent sulfur percent limit, determined weekly, remain and that an additional sulfur limit of 1.5 percent on an annual basis be added.

Sulfur dioxide emissions per million BTUs are primarily driven by three things: Removal efficiency, sulfur content, and BTU content.

As we consider the proper emission

limits, we must look at technology, at what removal efficiencies may reasonably be expected. We need to look at other emission limits. We must consider what others have done and we must look at fuel.

Dominion has advised us that the facility will be a state-of-the-art CFB facility. It has been touted as one of the best.

Some have proposed that we require IDCC or PC. These are alternatives that are properly considered.

Dominion argues that its plant can do as well in limiting emissions.

After looking at the data, and what a CFB can reasonably be expected to do with clean fuels and appropriate limits, I think Dominion makes a point -- with proper limits and reasonable fuel, it should do well.

Also, the CFB gives the company more continuous flexibility in the coal it burns.

Let's begin by looking at removal efficiency.

DEQ staff provided the board with a list of plants evaluated for S02 BACT.

This list included removal efficiencies.

These stated removal efficiencies ranged from 90 percent to 98.9, with two-thirds of the listed items at 98 percent and above.

With respect to the Wise County project, the staff calculated the removal efficiency, given the emission limits it proposed. DEQ calculated these emission limits to be 98 percent for using run-of-mine coal, 98.4 percent for waste coal only, and 98.1 percent for a blend of run-of-mine and waste coal.

Then staff states that it developed a 30-day S02 emissions limit on the basis of a 98.8 percent removal efficiency for waste coal only.

Staff puts the 30-day limit at 75 percent of the 24-hour limit of .12.

It is important to note that on the BACT list, four plants were listed with removal efficiencies of between 98.7 and 98.9 percent.

Staff discussed a number of these plants. Staff does not discuss, although it lists the AES Puerto Rico plant that was in the BACT list, staff calculated at 98.3 percent removal efficiency.

This 98.3 percent removal efficiency does

not reflect what the AES plant can do, has done or is now doing.

The AES Puerto Rico plant was originally permitted in 1998. Its only S02 limit is a three-hour, .022 pounds per million BTU limit. The stack test was conducted in 1902.

The sulfur dioxide emissions for Unit One were .00037 pounds per million BTUs.

For Unit Two, they were .0013 pounds per million BTUs.

The stack test report was examined by EPA, and it noted concerns, but not with respect to S02.

A second stack test was performed for these other areas. No retest was deemed necessary for S02, and EPA reported that the S02 stack tests results were entered in the areas database.

The EPA's summary of emissions compliance test results specifically reports that the S02 removal efficiency of Unit One was 99.8 percent and for Unit Two, it was 99.3 percent.

We requested CEMS data for AES and received it for a quarter in 2003, one in 2004, part of 2007, and the first quarter of 2008.

The data for the 2003 quarter showed Unit One, 30-day average emission ranging from .004 to .007, with most of the period in the .004 and .005 range.

Unit Two ran from .006 to a high of .015.

The data for 2004 ran from about .07 to .013.

We have CEMS 30-day average emission data for the fourth quarter of 2007 and the first quarter of 2008.

The S02 emissions at AES rose over time from about -- from where they began, to about .015 pounds per million BTU on a rolling 30-day average basis. That's understandable. The limit is a three-hour limit at .022 and the company is running the plant to meet the requirement.

While there was some exceedances of the .022, three-hour limit, they are reported to be related to start-ups, shut-downs and other unusual events.

I looked at the AES data in some detail for the fourth quarter of 2007 and the first quarter of 2008, where we have sulfur content, BTU data and 30-day average emissions.

For these areas, emissions ran from about .013 to .017 pounds per million BTU, with the vast majority being at .015.

Removal efficiencies --

(Whereupon, telephone contact with John Hanson was lost, and a short recess was taken while telephone contact was re-established.)

MR. MOORE: For these periods, the last quarter of 2007, and the first quarter of 2008, emissions for S02 on a 30-day rolling average basis were basically .015 and removal efficiencies were 98.7 and 98.8 percent on a very consistent basis.

So this plan has been reported by EPA to have removal efficiencies of 99.3 to 99.8 percent removal efficiencies, and it is now running at 98.7 and 98.8.

The Wise County plant is state of the art. It is certainly reasonable for this board to consider removal efficiencies that include not only those in the high 98s, as referenced by staff, but also those 99 percent and above.

Next we must consider fuel sulfur and BTU content.

Company and staff tie the emission limits

to run-of-mine coal at 2.28 percent sulfur, at about 7800 BTUs per pound, and one percent sulfur coal with BTU below 2800.

Staff fails to consider other cleaner fuels because it finds, quote, requiring the use of alternate fuels would redefine a fundamental aspect of the project, which is designed to burn Virginia coals and waste coals consistent with incentives provided by and in the public interest established by the Virginia General Assembly.

With all due respect, burning clean coal also is consistent with these incentives, and clean coal also complies with Virginia's environmental laws and regulations, and the Clean Air Act.

Finally, of course, even if there were to be a specific requirement related to Virginia coal, it could not trump the Clean Air Act and our obligations under the Clean Air Act.

The company argues that it should burn waste coal and run-of-mine coal because it is good for the environment.

It says burning waste coal would reduce waste coal piles that are polluting streams.

Burning run-of-mine coal could avoid waste coals that results from washing and processing coal.

I know the governor's recent letter to us does not intend to suggest that we should not consider these arguments.

While burning waste coal can provide an environmental benefit, if the waste piles are eliminated, air pollution will certainly increase compared to using cleaner fuels.

Emission limits should not be set based on waste or run-of-mine coal. We should allow waste coal to be burned only if emissions are held to a proper level, based on clean coal.

In addition, the board should approve any plan to burn waste coal piles, including which piles, and the right to require that if a waste pile is to be burned, that the board could require that all of the coal either be burned or safely stored.

Now, let's turn to the Clean Air Act.

Yesterday, which seems fairly long ago, we heard much about the rule of law and how we should obey the law.

The Clean Air Act is the law. Under the

act, MACT, quote, means the emission limitation based on maximum degree of reduction, which the permitting authority determines is achievable through application of available methods, including: Fuel cleaning, clean fuel or treatment.

That is our obligation and our duty. They have argued that requiring a company to use the cleaner coal would redefine the fundamental aspects of the project.

It cites an Environmental Appeals Board order of August 2006 in in Re Prairie State Generating Company in support for this decision.

That decision was appealed and the decision for the Seventh Circuit is instructive on the issue of cleaner fuels.

The Circuit Court found that the plant was a mine-mouth plant, and requiring the generators to give up that aspect of the facility and use alternative fuels would involve a redesign that was not required.

This is, of course not a mine-mouth plant.

The Court then speaks directly to the

issue here, requiring low sulfur coal, rather than high sulfur coal.

The Court recognized that adjustment in the design of a plant would be necessary to change the fuel from high sulfur to low sulfur coal.

The Court then concludes: If it were no more than would be necessary whenever a plant switched from a dirty to a cleaner fuel, the change would be the adoption of a control technology. Otherwise, clean fuels would be read out of the definition of such technologies.

The decisions of the Environmental Appeals Board also speaks to clean fuel.

They make clear that technology and percent reductions are not enough. Cleaner fuel must also be considered.

In Indeck-Elwood, the board reviewed this issue with statements and quotes as follows: In determining BACT, the permitting authority must assess for each pollutant the maximum degree of emissions reductions achievable through application of production processes and available methods, systems, and techniques,

including fuel cleaning, clean fuels or treatment, considering various factors, such as energy, environmental, and economic impact.

The board has consistently held that in deciding what constitutes BACT, the agency must consider both the cleanliness of the fuel, and the use of add-on pollution control devices. Thus proper BACT analysis must include consideration of cleaner forms of a fuel proposed by the source.

And that is what DEQ has done in the past.

For example, in Mecklenburg, the applicant proposed 2 percent sulfur coal, but was required to use 1 percent.

Various Federal and Virginia law require consideration of cleaner fuels that can help maximize the degree of reduction.

The question then becomes: What is clean coal in this case?

I looked at data from Virginia EGUs for the 2005 through 2007 period. There are not dramatic differences from year to year.

Looking at 2007, sulfur content ranges from about .53 percent to 1.26 percent for

Virginia's EGUs, according to data collected by DEQ staff.

Of the roughly 50 boilers, 37 burn coal that average less than .9 percent sulfur in 2007 and 17 use coal containing sulfur below .9 percent.

Dominion has six such boilers below .8 percent -- Alta Vista -- two boilers at .76. And of course, Chesapeake, four boilers running from .53 to .61.

Staff reports BTU content averaged over 12,500 in Virginia. In 2007, there were 27 boilers burning coal that averaged about 12,900 BTUs to 13,000 BTUs per pound.

About two-thirds of all of Dominion's coal came from Virginia in 2007. And according to staff and numerous others, there is plenty of high quality, low sulfur clean coal available in Virginia.

Clean coal can certainly reasonably include what Virginia EGUs burn in the last year or so from an economic and availability perspective.

Let's next turn to emissions limits.

We heard yesterday the staff statement,

or at least the suggestion, that this plant would be the cleanest in the nation. The proposed S02 limits certainly don't support that.

We see on staff's BACT list, six current limits below the .09 proposed by staff for this Wise County plant -- Spiritwood Station at .06, Deseret at .055, Gascoyne and Highwood at .038 and AES Puerto Rico and Nevco are at .022.

Also, interestingly, in Virginia, four power plants have emissions below the .09 pounds per million BTUs, proposed for this new plant. They are: Alta Vista, Churchwood, Clover and South Hampton.

I have proposed a rolling average of .022.

While this plant has stated that it is designed to burn up to 20 percent renewable or biomass, we have just heard that they are not comfortable with that. They are going to have to start out with a little less and work their way up.

I think as we begin this, we must consider biomass. We must, when we say we are going to set S02 limits -- all of that can't be

-- doesn't have to be, if you will, head room or leeway.

Now, looking at this, how might Dominion meet the .022 limit, considering biomass?

Staff BACT limits lists four plants with removal efficiencies at or above 98.7 percent.

AES Puerto Rico limit is .022, and that is a three-hour limit. We're going to use it as a 30-day limit.

AES Puerto Rico has achieved .013, .017 and has consistently had removal efficiencies at 98.7 and 98.8 percent.

Even at those modest limits, applied to 1 percent sulfur with a BTU content of 12,400, achieves the .022 pounds per million BTUs for Dominion without even considering biomass.

.022 pounds per million BTUs is clearly achievable by the company, even burning 1 percent sulfur coal.

The company has also not shown that using 1 percent -- 12,400 BTU coal is not feasible. Dominion's cost analysis, such as it was, does not support the conclusion that the fuels needed to meet the limits are either infeasible or cost prohibitive.

First, the cost of what we might call the "chosen fuel" or the "base case," was not based on market prices, but rather determined by a consultant based on market information.

Why? Because the 2.28 percent run of mine coal was non-standard.

More importantly though, the company said that 2.8 percent coal was quote, its worst case, and, quote, does not necessarily represent the fuel product that will be used in the day-to-day operations.

So we don't know that the base case is the base case.

Second, the alternative coals that the company chose to price, range, as we heard this morning, from .09 percent to .75 percent sulfur coal.

As we have seen, the limit can be met with 1 percent sulfur, without considering biomass, even if we have the relatively modest removal efficiencies of 98.7 or 98.8.

A removal efficiency of 98.9 or 99 percent should be a worst-case scenario based on what we know from the stack tests and CEMS data at AES Puerto Rico and other facilities.

If the Dominion plant really is state of the art, and even comes close to the AES removal percentage of 99.8 percent, then we can certainly expect it to achieve 99.5 percent.

If it just gets that close, the company can burn almost all waste coal, and if, as we heard yesterday, the waste coal is .5 percent sulfur, rather than 1 percent, the company could burn 100 percent waste coal and still keep the S02 emissions below .022.

So we have annual emissions would be below 604 tons, and waste piles could be eliminated.

The limits I propose allow the company to build the CFB plant it requests. Fuels to achieve the limits, even at modest removal efficiencies, are readily available and reasonably priced as demonstrated by the fact that they are used by Dominion and other EGUs in the Commonwealth today.

With these fuels, they can meet the limit. And if the limit -- if the removal efficiencies achieves even close to AES Puerto Rico, the company can burn waste coal as well and the waste piles can be eliminated.

MR. LANGFORD: Thank you.
Mr. Buckheit.
MR. BUCKHEIT: Thank you.
I come at this just slightly different from Judge Moore, but I'm more of a hardware guy.
And I have had the experience with these kinds of units for a number of years, and I've talked to the people in region two who built the AES Puerto Rico permit and I have talked to the people down in Puerto Rico who monitor the performance of the unit.
And in my April memo, I pose the question: Is it the permit or is it the project?
I have said earlier, that what Dominion has proposed is the full up suite of controls. It is the best there is.
But what a number of people don't -- haven't got caught up with, is the fact that over the last ten years in particular, the performance of pollution control devices in this country has really gone forward to another order of magnitude.
Today's controls can do a whole lot

better than what was in use even ten years ago.

In those days, we were wondering: Well, we started out with S02 scrubbers in the '70s at 70 or 80 percent and then it became 90 percent and then it became 95 percent, and then we moved to 98 and then we go to 99 percent controls.

For PM, we see we have gone well past the 99 percent threshold and we are now at 99.5, 99.7, 99.9.

Similarly with NOx removal, ten years ago, we were looking at 80 percent, and now it is 95.

So the performance of these control devices have really improved over the years.

I am personally convinced that the suite of controls that Dominion is proposing can meet these limits while burning virtually any coal that we're talking about.

There may be a couple of seams in the area that they might have to blend to use, and there may be a couple of seams that they can't use.

But by and large, I believe when I asked the question, you know: Can the technology get

us to the point where we don't care whether we burn run-of-mine coal, whether we burn waste coals?

And I come out of this process saying: Yes. The controls that Dominion is proposing, I believe can meet these limits while burning waste coal and run-of-mine coal and gob.

And we are not proposing here today to limit Dominion from burning those materials. Nor are we proposing today to require Dominion to wash its coal.

While that could be a control technique that we could order them to do, as the top control strategy -- again, even without washing, I think that -- I am convinced that these controls can meet the limits that we're proposing here today.

We have provided a couple of areas of head space. The AES permit limit is a three-hour limit -- the 022 -- which normally would mean that on a monthly basis, you could probably be at something like 019. And we have instead proposed an O22 monthly limit, rolling 30 days. And that is putting a little head space into the system.

It's important for people to understand that the issue of setting permanent limits is not just to drive down the number as low as possible.

If I didn't think Dominion could meet these limits, I would go in the other direction. I would say: You can't burn unwashed coal. You can't burn gob.

Because, if I were to invent a fairy tale limit that I didn't think the company could meet, it might look good on paper. The facility would get built, and then the system would react, as it has to, and it would relax the limit.

And so we would basically be defrauding the public. I am not going to go there.

On the other side, if the limit is too loose, what happens is that, as we see in the AES data and as we saw in the Merit data, if you create too much head space, you -- the company is naturally concerned, you know: Gee, can I make this limit?

And I understand that and I don't fight that. But I have a different balancing act to take.

If the limit is too loose, then the company doesn't have to fully employ the technology that it has built. Both with ACI and with the absorbent technologies, you have an operating cost associated with injecting absorbents.

If I provide a limit where this overly generous amount of head space -- most times that head space gets eaten up, even though there is no technical reason for it.

So we see, for instance, with AES in the early years, they were running at 004 and 005. Currently, they are running around 015. They have tripled their emissions.

Now, I have drilled into it, but on my experience over the years, I read that as them simply tying their system in to make sure that they have a compliance module under that three hour 022, but otherwise, there is no law that requires them to operate down at 005, and, you know, Puerto Rico winds up with the health effects that are associated with not being as precise as you can with the emissions.

So I view our job is to try to get it right -- neither too high, nor too low. And I

think O22 is right.

Thank you.

MR. LANGFORD: I am actually still trying to come at this from yet a little bit different angle.

Mr. Moore, you had read, I think at the beginning of your statement, the definition of Best Achievable Control Technology BACT.

MS. THOMSON: He read part of it.

MR. MOORE: I read part of it.

MR. LANGFORD: Can you read that again?

MR. MOORE: You have got to have some ellipsis points or you can't -- you have to take deep breaths.

MR. LANGFORD: Or if you can hand it to me, I can read it.

Do you have it handy?

MR. MOORE: Well, I have got a copy of it here somewhere.

MS. THOMSON: I think he wants the first part here, the long sentence.

The best available control technology means an emissions limitations, including a visible emissions standard, based on the maximum degree of reduction for each regulated

MSR pollutant that would be emitted from any proposed major stationary source or major modification that the board on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such source or modification for the application of production processing or available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of such pollutants.

MR. LANGFORD: That's enough. I got what I needed.

MR. BUCKHEIT: You left out cleaning fuel.

MR. LANGFORD: She read it.

Where I am coming from, as a guy that used to be in industry, and I have been looking at regulations -- when you start the permit, you need to look at -- it is a BACT permit -- it is a B-A-C-T permit.

So what do you do?

And what this shows is that it's the maximum degree of reduction. In other words,

maximum control efficiency, if you will, is what the best available control technology is. I have looked at some of these numbers, and I don't have them in front of me. One of you can point to the actual degree of reduction at AES Puerto Rico. I think you quoted them, Mr. Moore.

MR. MOORE: 98.7 and 98.8.

The test is 99.3 and 99.8.

MR. LANGFORD: 99.3 and 99.8.

There is an argument that that is -- or could be the maximum achievable reduction -- maximum degree of reduction for S02 in a comparable plant. It's a CFB with the flue gas desulfurization.

In looking at the numbers that were presented earlier today and the numbers that were proposed in this amendment, which I have underneath here somewhere -- the -- in order to achieve the 603.6 annual tons, which is actually going to be pretty much expressed as a 30-day rolling average, and looking at what we have on the board here earlier as to the -- those eight scenarios, the different fuel mixes -- the first four were the ones considered by

DEQ, 100 percent waste coal, 60 percent waste, 40 percent run-of-mine, and then, flip that, 60 percent run-of-mine, 40 percent waste, and 100 percent run-of-mine coal, all at the proposed levels, the control efficiencies that would be required to meet the full amount of what was proposed, by my math, if I did it right, is for the first two, for 100 percent waste or 60 percent waste, 99.7 percent emissions reduction.

For the 60 percent run-of-mine or 100 percent run-of-mine at 2.28 percent sulfur coal, in the run-of-mine, it would need to achieve 99.6, and the AES numbers -- Mr. Buckheit --

MR. BUCKHEIT: 99.8.

MR. LANGFORD: 99.8 and 99 point --

MR. BUCKHEIT: Three.

MR. LANGFORD: Three.

MR. BUCKHEIT: Two units.

MR. LANGFORD: Two units.

MR. BUCKHEIT: But the difference is the information that Mr. Warren has gathered and the information that we got from our tour is that 2.28 percent sulfur is not --

MR. LANGFORD: I am not worried about what the tour is.
MR. BUCKHEIT: There is nothing in the record.
MR. LANGFORD: I understand.
MR. BUCKHEIT: Even Dominion says that the 2.28 is --
MR. LANGFORD: Let me make my statement then the committee can discuss it.
My point here is that even at the four scenarios that were considered by DEQ and were proposed by the company, it appears to be reasonable, based on actual degree of reduction at AES, that they could, in fact, burn the mixes of fuels that they had proposed and still achieve the 603.6 -- if I remember right -- level.
Now, obviously there is -- we have talked about there is some room in here because the actual run-of-mine coal might not be quite 2.28, et cetera, et cetera, but I do believe that -- it appears to me that the AES Puerto Rico does set or establish a maximum degree of reduction for S02s for this situation.
Now, moving on to the next item from the

department's presentation this morning is that, we identify the control technology, if you eliminate any technically infeasible options -- and I don't see anything technically infeasible between the AES Puerto Rico equipment and what was proposed for Virginia City, so I don't see that we are throwing it out from a technically unfeasibility option.

And then you establish the emission limits. And the emission limits for this, for AES were 0.22.

So I do -- I think I am to the point of agreeing with my colleagues that the .022, at least for today's conditions and the conditions requested in the permit, do meet the definition of Best Available Control Technology, which we are required to put in the PSD permit, and as well, allow the company to run the fleet of fuels that they had proposed in the project.

And so that was my analysis of this situation.

Ms. Thomson, did you have some comments?

MS. THOMSON: I have a few prepared comments that back up a little bit to first -- recall some of the general landscape here.

At our March 20th meeting we voted to assume direct control over this permit after 1500 members of the public asked us to do so.

While most permit applications -- air permit applications are handled by DEQ under authority delegated by the board, this permit application not only attracted a great deal of public attention; it presented complicated issues involving air pollution effects on public lands, the express desire of the Virginia General Assembly for Dominion to locate an electrical generating facility in Southwest Virginia and to use Virginia coal, emissions of toxic air pollutants like mercury and high greenhouse gas emissions.

Given the high profile and complex nature of this permit application, the board included an extra call for input. We have had an extensive comment period. We have had extended comment periods. We organized a special additional opportunity for the public and Dominion to comment on our questions that were posted online for 30 days, on the DEQ website starting in mid of April.

As a result of this unusually thorough

information gathering, hundreds -- maybe thousands -- I don't know, but certainly many many many written and oral comments have been received. The public record on this application is extensive.

As the Clean Air Act requires, the United States, the USDA, the Forest Service, and the National Park Service were offered early opportunities to provide formal comments on the proposed facility and to assess the possible impact on nearby federal and public land.

I believe in adopting the amendment that my colleague has proposed, that we are acting in accordance with our duly adopted regulations and regulatory processes.

We have not only been mindful of our specific regulations, which I will go into in a minute, but also of our overall statutory charges under the Virginia Code.

And they are: The board in making regulations and approving variances in coal programs and permits, and the courts, in granting injunctive relief under the provisions of this chapter shall consider facts and circumstances relevant to the reasonableness of

the activity involved, and the regulations proposed to control it, including, first, the character and degree of injury to or interference with safety or health or the reasonable use of property which is caused or threatened to be caused.

Second, the social and economic value of the activities involved.

Third, the suitability of the activity to the area in which it is located,

And, finally, the scientific and economic practicality of reducing or eliminating the discharge resulting from such activities.

Let me talk specifically about our rationale for heading in the direction that my colleagues have just outlined on the sulfur dioxide.

We have already heard a bit about the definition of Best Available Control Technology, which not only articulates a number of considerations with respect to looking at other facilities and evaluating their technologies, fuel type, and so forth, but also instructs us to take into account energy, environmental and economic impacts and other

costs.

According to EPA's guidance on determining BACT, a top-down BACT approach is required, all available control technologies should be identified and ranked in descending order.

The most stringent technology is established as BACT, unless the applicant can demonstrate convincingly that the technology is not achievable.

The choice of BACT is not left to the applicant, but rather should be set by the permitting authority at the most stringent level for which adequate justification for rejection was not provided.

But there are additional requirements for new major sources locating in what we call PSD areas -- prevention of significant deterioration areas, which of course applies here.

The program was intended to make sure that clean air stays clean. That is clean air area -- that areas with air quality better than the national or as defined as a clean air area -- let's put it that way -- that areas with air

quality better than the national ambient air quality standard, or NAAQS, should not be degraded to bear compliance with the standard.

In a nutshell, PSD requires a continued or expanded major commitment of a facility for clean air areas used, BACT, for minimizing air pollution. The program also establishes increments that limit the cumulative increase in pollution levels over baseline concentrations in clean air areas.

Through computer modeling, a permit applicant must demonstrate that the additional pollution it will produce can be accommodated within the available increments, and the source must also demonstrate that pollution will not cause or contribute to a violation of any national ambient air quality standard.

The Federal Land Managers are especially integrally involved in evaluating the effects on public lands because of the way the Clean Air Act sets forth their responsibilities.

Under Federal and Viginia law, Federal Land Managers must be notified of a permit application so they can assess a source's potential impact on what are called "Class One

Area," air quality related values.

In point of fact, the board may not issue a permit if the board concurs with the Federal Land Manager's demonstration the an AQRV would be adversely affected.

We do not have any determination of an adverse impact here. I have to say that up front.

DEQ and the board received comments from the Forest Service and the National Park Service on the Hybrid Energy Center's potential impact in increment consumption, and on AQRV. And I'll just talk a little bit about that.

I refer to my colleague, Mr. Moore's comments for the technology analysis in which he has well articulated the basis for the standards that we proposed in our minutes that are based on removal efficiencies, and sulfur levels in fuels according to the criteria that he set forth.

Let me talk a little bit about increment consumption.

The National Park Service has expressed an ongoing concern over potential violations of the S02 increments and AQRV impact on the Great

Smoky Mountains National Park.

These concerns were provided early. We received recent comments that were received outside of the regular comment period because the Park Service was unaware of a comment period that happened, an extra comment period between April 15th and May 15th, but they don't add -- they reinforce their concerns at this time.

They say that modeling conducted by the applicant indicates that a proposed 24-hour S02 emission would significantly impact both S02 increment and visibility at Great Smoky Mountains National Park, a Class One area administered by the National Park Service.

We continue to believe that there are technological solutions to those problems, either through the use of IGCC, or by making more effective use of proposed S02 control technology.

So making more effective use of proposed S02 control technology is one alternative that the Park Service puts out there for addressing its ongoing concerns with the S02 emissions from this facility.

State and federal regulations, as I have already indicated, direct policy makers to -- also to look at energy environmental and economic impact on other costs.

In this, I am going to briefly outline some of the environmental considerations that have factored into our consideration of BACT.

Specifically, we have expressed an ongoing concern as have many commenters over the impact of sulfur dioxide on already seriously degraded streams in nearby national parks and wilderness areas.

Sulfur dioxide emissions, of course are transformed in the atmosphere into acid precipitation, which causes a number of adverse environmental impacts -- adverse effects to humans as well as their effects on nearby ecosystems.

While national emissions of sulfur dioxide are declining, and while some ecosystems, especially in the northeastern United States show signs of biological and chemical recovery because of reduced sulfur depositions, many streams in the southern Appalachian are not recovering.

For example, the US EPA says in its most recent Acid Rain Progress Report that as far as stream chemistry is concerned, quote, sulfate concentrations are declining substantially in all but one of the regions in the Southern Appalachians. However, sulfate concentrations are increasing because this region is unusual because its soil can store large amounts of sulfate deposited from the atmosphere. Only after large amounts of sulfate have accumulated in the soil do stream sulfates concentration begin to increase, remaining elevated until the stored sulfur is depleted.

This phenomenon is now being observed in the southern Appalachians despite decreasing sulfate in the atmospheric deposition.

Of particular concern today are acidified streams or heavily impacted streams in nearby national park and national wilderness areas, several of which are seriously acidified and are thought to need continuous reductions in deposition before they will start to recover.

Scientists believe that many soils in the southern Appalachians are saturated with sulfur and will need continuous reduction in

depositions for those systems to recover. The forest service has flagged its concerns -- for example over the low acid neutralizing capacity of streams in Linford Gorge, saying again, in a nutshell that the accumulation of sulfur over time has built up in the soil banks, and that it will take much more reduction in deposition over time for these ecosystems to recover.

MR. LANGFORD: Before I get to Mr. Buckheit, two quick points, let me make -- I'll give John, over the phone, an opportunity if there is anything that you want to add that you may not have heard already that you want to add or you may already be okay with what has been presented.

John, do you have anything?

MR. HANSON: No, I don't have anything to add, Richard.

I would like the people to know, however, that even though I can't be there in person, I have read carefully the briefing book that the DEQ staff has prepared, which included, of course, all the public comments, and I have been paying close attention to the information that I have heard this afternoon.

I have, however, nothing to add at this time.

MR. LANGFORD: Thank you.

Mr. Buckheit, did you have --

MR. BUCKHEIT: Yes. Just three sort of factual matters.

One is, if we were to set precisely based on the AES Puerto Rico, the 30-day rolling average, my number would be something in the range of .006.

In moving up to 022, we would be recognizing the fact that AES Puerto Rico burns very low sulfur coal, and providing ample head space, I believe, for the increased sulfur content of both background Virginia coals plus these coal wastes that Dominion might want to burn, while still recognizing the superior performance of a CFB SDA unit.

And let me explain it to the folks.

A circulating fluidized bed boiler contains limestone in the bed that's suspended in the air as the fuel is fed into it.

That limestone naturally reacts with the S02 coming off the combustion process. And it itself is a control device. And that's why CFB

is recognized as a clean coal technology.

Typically 90 to 92 percent of the S02 is removed right there. It is absorbed into the limestone in the bed, and then winds up in the ash pile.

What Dominion is proposing -- and for many years in this country -- even currently in Europe, CFB without a follow-on control device -- that is it. That's all you need.

What Dominion is proposing is to follow this control device with what is called a "spray dryer absorber," which can get 95 percent of what remains.

And that is why -- if you multiply 90 times 95, you can get these very very low removals.

In the comments, Dominion has said: Well, they are only currently intending to design their CFB for 80 percent removal.

And that is well below what's recognized in the literature as BACT for this kind of -- I don't want to say BACT -- it is what this technology can achieve itself.

So in my own mind, in calculating the efficiencies -- and this is how you see these

very high efficiencies being reported in the field -- you have two highly efficient devices acting in series.

Thirdly, there is an issue about costs. I just want to mention that I do not accept or find at all convincing Dominon's cost calculation with respect to run-of-mine coals versus other coals. I think Mr. Moore hit most of it, but I don't recall whether he addressed the figures that we received when we visited the coal washing plant.

I had asked in my April memo, not what are the market prices, because those markets can vary over time, but what is the cost of doing this?

My assumption is that over a long period of time, the difference between the price of washed coal and unwashed coal in the market should stabilize out as BTU plus costs of doing this.

And we were advised by the CEO of the coal washing firm that the cost was three to seven dollars per ton, or three to eight dollars a ton.

This is far less than what was suggested

by Dominion's cost analysis.

Thank you.

MR. LANGFORD: May I make a clarification --

MR. BUCKHEIT: I say that, but it is mostly irrelevant because we are not -- in making this decision, we are not requiring coal washing.

MR. LANGFORD: One point -- I guess, just for the record, clarification, I believe Mr. Moore, in your motion, your .022 number comes from the permit limit at AES Puerto Rico and others?

MR. MOORE: Yes. It is existing in two other places.

MR. LANGFORD: And the 24-hour average and three-hour average numbers that we proposed in this amendment are essentially scale-ups -- a ratio -- the same sort of ratio that the staff's original three-hour and 24-hour numbers were done.

MR. MOORE: That's correct.

MR. LANGFORD: So the .12 and .15 limit and I think the calculations started with .022 and just sort of used the same sort of ratios

to raise them up to a 24-hour and 30-hour average.

MR. MOORE: That is correct.

MR. LANGFORD: Is there other discussion on the motion?

Seeing none, we will call for a vote on the motion.

I'm sorry. Mr. Paylor?

MR. PAYLOR: (Undiscernible.)

MR. LANGFORD: I was about to say -- well, I will restate the motion.

It is an amendment to the original motion and it is to change Condition 29, of Emission Limit in the draft PSD permit.

MR. MOORE: Do you want me to read it?

MR. LANGFORD: I think I have got it right here.

If I have get anything wrong, you correct me.

Provision 29, Emission Limit that appears on pages eight and nine of the draft PSD permit, page nine has the sulfur dioxide limits. It shows a combined total tons a year limit, and the new combined total tons a year limit is 603.6. The three-hour average for

each boiler in pounds per million BTU, 0.35.

MR. MOORE: No.

MR. LANGFORD: Three-hour average.

MR. MOORE: Oh, I'm sorry.

MR. LANGFORD: I'm reading down instead of up.

MR. MOORE: No, no. You are doing pounds per million BTU.

MR. LANGFORD: Right. .035 pounds per million BTU with the staff to do the math to make that into pounds an hour, and we'll get to that. That's at the bottom.

And the 24-hour average is .029, with the staff to calculate the pounds per hour for each boiler, and the 30-day rolling average, .022 pounds per million BTU, again with the staff to add a pounds per hour number for each boiler.

MR. FEAGINS: No. We will prepare a pounds per megawatt hour, for the 30-day rolling average.

MR. LANGFORD: It was instead of pounds an hour?

MR. FEAGINS: No, I don't think that there is a --

MR. LANGFORD: Well, there --

MR. FEAGINS: No. I was simply adding a pounds per megawatt hour for a 30-day rolling average.

MR. LANGFORD: So that will be a new column -- Rob -- it will be a new column -- pounds per megawatt hour, not pounds per million BTU, but pounds per hour.

MR. FEAGINS: Gross. That was my question.

MR. LANGFORD: Was your question whether it should be net or gross?

MR. FEAGINS: Yes. That was my question. I was advised.

MR. LANGFORD: I would like to do net, but she advises me that you-all did gross all the time.

MR. FEAGINS: That's correct.

MR. BUCKHEIT: The permitting authorities like Massachusetts that do it -- what do they do? We just want comparable.

MR. FEAGINS: I can't tell you.

MR. BUCKHEIT: Just research about it, whatever is standard in permitting.

MR. MOORE: If there is a standard in the industry, one significant that outnumbers all

others, do it that way.

MR. LANGFORD: Would you like to make a comment?

MR. JOSEPHSON: Just for record, sir -- I think when you read the three-hour average, you said 3.05 and I think you meant .035.

MR. LANGFORD: I did mean .035.

MR. FEAGINS: You're correct.

It is .022, .029 and .035.

MR. LANGFORD: And what I am unclear about is your output based number --

MR. MOORE: That will be pounds per megawatt hour, and the staff will look and if there is a --

MR. LANGFORD: Let's decide on how we want it.

MR. MOORE: I would like to be able to compare it to other states, and if all states but us do it on net, I'd like to do it net. You know, if it is kind of half and half, then we can do what the staff has been doing.

MR. LANGFORD: The number will flow from .022. You have all the information you need to determine the number with the .022, once -- if it is all gross or net.

MR. FEAGINS: The staff has informed me that the documentation that we have univerally indicates gross and EPA uses gross, although our research is not exhaustive.

But everything that we do have indicates gross.

MR. LANGFORD: It will be consistent with everything that you have done?

MR. FEAGINS: That's correct.

MR. LANGFORD: Gross. We will do gross.

MR. MOORE: All right. Go ahead and do gross.

MR. LANGFORD: And the motion also suggests or encompasses the removal of Paragraph 41, Source Reduction Remission Offsets.

MR. FEAGINS: That's correct.

MR. LANGFORD: And appropriate renumbering or whatever is needed.

Is that a correct statement of the motion?

MR. MOORE: As long as the numbers are right and I think we have said them enough.

MR. LANGFORD: Any further discussion on the motion?

We will do a roll call vote.
Mr. Moore?
MR. MOORE: Aye.
MS. THOMSON: Thomson, aye.
MR. LANGFORD: Mr. Buckheit?
MR. BUCKHEIT: Mr. Buckheit, aye.
MR. LANGFORD: The Chair votes aye.
Mr. Hanson?
MR. HANSON: Aye.
MR. LANGFORD: That motion is carried.
We have one amendment agreed to, to the original motion.
MR. MOORE: Mr. Chairman, the other two I had -- I don't think they are -- they are non-controversial, I think. They deals with the --
Go ahead. Mr. Buckheit wants --
MR. LANGFORD: Mr. Buckheit, do you have --
MR. BUCKHEIT: I move to amend the MACT permit to substitute a .090 pounds per trillion BTU referenced in the --
THE REPORTER: I'm sorry. I didn't hear you. Could you move your computer?
Okay. Now start all over.

MR. BUCKHEIT: I move to amend the mercury limit in the MACT permit to a figure of 0.90 pounds per trillion BTU on an output basis.

MS. THOMSON: Second.

MR. BUCKHEIT: Output.

MR. LANGFORD: Let me have you point to the particular draft permit page and condition, if you would.

I know that we need to make this clear. I think you are referring to the emission limits on Condition 13?

MR. BUCKHEIT: Yes.

MR. LANGFORD: That condition currently has for a limit for each boiler, in pounds per million watt hours -- megawatt hours -- thank you -- and the number being .0000014, which is the number we were referring to earlier. It also -- that current condition now has a combined total tons a year of 8.19 pounds per year.

And tell me again, Mr. Buckheit, what you're proposing to change this number to?

MR. BUCKHEIT: I'm proposing to delete the 8.19 pounds per year.

I am proposing to have a limit of 0. -- I'll read it right here -- nine zero pounds per trillion BTU, and have that limit expressed as well on an output basis. And that number would be complied with on a rolling annual average basis.

MR. MOORE: Mr. Buckheit, I am having difficulties.

MR. BUCKHEIT: I said pound per trillion BTU.

MR. MOORE: But just -- give me -- assume I have a 1.4. This is a .9?

MR. BUCKHEIT: This represents approximately a one-third reduction from the other.

MR. MOORE: So if the other is 1.4, this would be .9?

MR. LANGFORD: The units are different from what he quoted and what you're looking at.

MR. MOORE: I understand.

MR. LANGFORD: But more or less.

MR. MOORE: Well, I think it has to be consistent.

MR. LANGFORD: Well, the units are different. He's quoting -- the units of the

limit would change from an output basis to potentially --

MR. BUCKHEIT: I am asking the staff to convert it back, but we're starting with --

MR. FEAGINS: Oh, you're doing it per megawatt hours?

MR. BUCKHEIT: No. I am doing it per trillion BTU. So we don't get into the ten to the six and seven.

MR. LANGFORD: Correct. But my point is the current limit is not on a BTU basis. It is on a megawatt hour basis.

MR. BUCKHEIT: Well, the comparable number is something like .149 pounds per million -- per trillion BTUs.

Is that good, Staff?

.149 -- and I am suggesting about a third less -- .09.

MR. FEAGINS: Are you suggesting then to recalculate the megawatt hour number based on this new number?

MR. BUCKHEIT: Yes.

MR. FEAGINS: Or are you suggesting to change the currency of the limit from output to input?

MR. BUCKHEIT: I would like it to be expressed both ways, so people in the outside world can understand it.

They are in fact identical limits because it would be based on the same rate of heat.

Am I correct, Mr. Dowd?

MR. DOWD: Yes, Mr. Buckheit.

MR. BUCKHEIT: You can put it in parentheses, the information is the same.

But I am also suggesting that if you do it on a rolling annual average basis, we do not need to set an annual tonnage figure.

MS. THOMSON: And that corresponds roughly then? Do we divide it to the previous annual?

MR. LANGFORD: We haven't had a second yet, as I recall it.

MS. THOMSON: I already seconded it.

MR. LANGFORD: I still would like to make sure I understand what is going to go into the document.

Right now it appears the document has a pounds per megawatt hour, and you would like it to reflect both pounds per megawatt hour and pounds per --

MR. BUCKHEIT: Trillion BTU.
MR. LANGFORD: Trillion BTU.
MR. BUCKHEIT: 0.090 pounds per trillion BTU.
MR. LANGFORD: And just for reference purposes, have you done a rough calculation of what that means for the combined total, if you're proposing to remove from the permit that was 8.19, just for information?
MR. BUCKHEIT: Yes. I've calculated that if the unit were to run at full load, but with a 90 percent capacity factor, so full load, 90 percent of the days, that would be 4.45 pounds per year, which is in the range of -- the DEQ's number was eight point something?
MR. FEAGINS: 8.19.
MR. BUCKHEIT: So, I don't know whether the DEQ put in the 8.19 capacity factor or whether they assumed it was --
MR. DOWD: We assumed it was the 8760.
MR. BUCKHEIT: And that, quite frankly is an overestimate because plants don't do that, nor do they run full bore, even 90 percent of the time, but that is my estimate is 4.45 pounds.

MR. LANGFORD: Okay.
MR. BUCKHEIT: And I would call that a worst case.
MR. LANGFORD: I believe that I now understand your proposal.
Would you like to open the discussion on this proposal?
MR. BUCKHEIT: Sure. Let me explain how I arrived at this figure.
This limit is based on the Reliant Energy Seward Station, which I believe all agree is the best performing similar source out there.
I recognize that there are questions about the data, but we will always have that in the regulatory process.
We are directed by the Congress to set these MACT standards based on the available data.
In fact, as one of the control processes -- I think states -- you either discard or you are not allowed to require stack testing of sources -- certainly 112-J will not allow it.
We have testing at this facility done three different ways, by a well respected state. Pennsylvania has one of the best

testing programs in the country, and contractors for the company.

And they each came to comparable, but not identical results.

I -- in pursuing my due diligence, I called the Pennsylvania -- the director of Pennsyvania Department of Air Quality. She got her chief of source testing on the line, and I cross-examined them as to whether they were standing behind these numbers.

I originally was a skeptic on these kinds of very low numbers for mercury.

I started warming to the process when I looked at -- back in April -- the very low results reported for other units burning coal waste in Pennsylvania.

There were five or six of them up there that were tested for purposes of developing a standard. And they were all testing very high removal numbers -- 99.2, 99.5, 99.7, but they were smaller units.

And so I noticed that this particular facility existed, and it appears to be -- it is roughly the same size as our facility with the same control techniques -- some of them.

Actually we have better. We have better technology proposed for Virginia City Hybrid Energy Center than what this very low facility has.

It is a CFB with an SDA. We have in addition to that activated carbon injection.

So even though -- and I accept the notion that it is outside the applicability limitation of ASTM -- and you heard me fussing about that this morning. ASTM is the American Society of Testing Materials -- or something like that. And they are a -- not a regulatory body -- they're an industry body that attempts to standardize testing procedures.

It takes years to get a new procedure through the ASTM process.

Meanwhile, there is lots of science that goes on outside the ASTM program, and lots of that science is entirely reliable.

And so when I see the State of Pennsylvania standing by their numbers with their experience, and I see that independent companies using different test methods run simultaneously on this plan, I am reasonably comfortable with it.

I am not totally comfortable. I am reasonably comfortable. This is the best number we have.

So what I did -- the results were three runs on the Ontario Power test method -- O2 -- excuse me -- 0.02, 0.01, 0.01. The average of those three is 0.13. I ran a standard deviation and computed the 98th percentile confidence level.

That turns out to be O258. That is one third -- less than a third of what I am proposing.

Similarly, I took the two test results that used the Method 324 testing. I computed the average of those two. I ran the standard deviation. And I looked at the 95th percentile confidence number, and I got .0339.

Again, about a third of what I am proposing.

That is where you would normally be, except I am taking standard deviations of relatively low numbers -- two tests, three tests.

And so what I did to add an extra measure of conservatism in it, is I took the highest

test result in this set, which is .03 and I multiplied it by the ratio between the highest result and the lowest result.

Now, I think most statisticians in the world would shoot me at this point, including Mr. Finto, but this is a very generous way of accommodating for uncertainty. It is conservative.

And so, multiplying the highest number by that ratio of the highest to the lowest, I get to .09 pounds per trillion BTU.

MR. MOORE: Mr. Buckheit, just so I can understand this simple math -- the highest number was .03. Your number is point .09. It is three times larger than the highest number.

MR. BUCKHEIT: The ratio of the highest number to the lowest number is .03 divided by .01, which is three, times the highest test, which is 03, as being .09.

MR. MOORE: But for those of us in Richmond, that's three times.

MR. BUCKHEIT: Yes.

MR. MOORE: I just -- I wanted to make it clear that you know that it was three times.

MR. BUCKHEIT: In addition -- I think

someone earlier mentioned the National Association of Clean Air Agencies. I think that Mr. Dowd did.

I served as a consultant to that group. That's the Association of the State Air Pollution Control Administrators over the past six months, helping them to develop air toxin limits for industrial boilers.

And we collected a lot of data and looked at issues like these, only it was a technical committee -- I think it was 17 members from state and local Air Pollution Control Agencies. Ms. Bonduri was on that, if she's here -- and at the end of that process, the technical committee recommended that in converting from test results to MACT limits for that program, a range of between one-and-a-half to two-and-a-half, and perhaps three was appropriate to take a stack test result and turn into a limit.

And so, sort of an independent group looking at similar issues came out with the same general ratio in terms of translating a stack test into a limit.

MR. MOORE: I just want to say, I support

this.

I do so based on the test results that we have seen and we cannot ignore the reality of other alternatives. We have to be careful. And I believe Mr. Buckheit, in laying his terms by multiplying that by three has been certain that this is a limit that is achievable.

I don't think we should refuse to set an appropriate limit because of -- our testing is not -- physically, we have some difficulties if there are alternatives, if we take the care to provide a safety factor there, and I think the way Mr. Buckheit has done that is appropriate.

And I support this.

MR. BUCKHEIT: I have to point out that this Reliant facility is burning 100 percent waste coal.

MR. LANGFORD: Ms. Thomson?

MS. THOMSON: Yes. I just have a point of clarification for Mr. Buckheit.

There was some mention in the public comments about this Condition 33 to allow adjustments of the standard later.

MR. BUCKHEIT: Yes. My recommendation -- there might be a subsequent motion -- it's not

in this one, but I believe it should be removed.

MR. LANGFORD: You're correct that it is not in this motion.

MS. THOMSON: I guess I would concur with the amendments. I think that the overall movement downward on mercury emission limits at this facility is quite appropriate given our very stringent directions under the Clean Air Act pursuant to MACT standards.

And as was indicated earlier today by DEQ staff, we are also directed under the Clean Air Act to consider non air quality benefits, one considering going beyond MACT.

The consideration I am about to mention now is more in the category of general consideration, monitoring quality -- a consideration that I think justifies the general movement downwards on the standard of tests that have to do with mercury deposition.

Of course, we have had an ongoing study in Virginia going on for -- I am not quite sure how long now -- a mercury conference to consider mercury deposition in Virginia's waterways and elsewhere in Virginia from air

pollution sources.

That study is not finalized. It is in the draft stage, so it is inappropriate to comment on it now, so I will refer to published literature that confirms that.

The Linwood coal-fired electric utilities emits mercury. A large portion of the emitted mercury is deposited within a short distance of these large sources.

This was based on work that has been done in the northeast that has been peer reviewed. We, of course, have to weigh the results of our own particular mercury deposition study, but based on what I have seen in the existing literature, the fact that we have pushed down on mercury emissions from the source will be good for reducing local deposition.

MR. BUCKHEIT: I must point out that the Seward station does not have activated carbon injection with a fabric filter for additional control. I would expect to see an additional 50 percent minimum reduction from activated carbon with that. And I think that provides an additional measure of assurance that -- or increases the confidence that these kinds of

limits can be achieved with the systems that have been proposed.

MR. LANGFORD: I come at this permit, obviously, again from a regulatory standpoint, from my background, and this is not a PSD permit, it is not a DAT permit, it is an MACT permit which is the Maximum Achievable Control Technology.

And on a case-by-case basis, the way this has been -- has to be set -- in setting this maximum achievable control technology, the permit agency in this case is required to look for the best controlled similar source. And we had a lot of discussion this morning about this particular plant in Pennsylvania, which I think has been agreed to be the best controlled similar source.

Where I differ from the staff's recommendation -- they had concerns -- rightfully so -- about the ability to accurately measure these low levels of mercury.

And there was significant discussion this morning about the applicability level of the test and how the -- we believe the applicability of that test is at 0.3 as opposed

to the .09.

In other words, it's significantly higher than that.

So the staff did have an amount of uncertainty, and for that basis they took a little different path to arrive at the number that they had in this current draft.

I understand that. However, I am looking at, you know, we're required to look at the Maximum Achievable Control Technology, and there is not a huge amount of data, but we have essentially three runs at one time, on this one plant, using two different test methods that all have extremely low mercury results -- the ones that Mr. Buckheit alluded to earlier.

I think this gives one a little bit more confidence that the numbers are extremely low from this plant.

And our MACT floor is to be set at the best controlled similar source. And where I come from is, these numbers look like they are actually achievable.

These aren't permit limits. These are what have actually been achieved in practice -- although not a lot of practice -- some practice

-- and therefore they do seem to me to establish the MACT floor for this -- for this unit.

And the analysis that Mr. Buckheit did to arrive, including variability, the case law and such, allow us, in fact require us to take into account in setting emission limits for MACT standard, the kind of worst case normal variability of those tests, which is sort of where he came from by using at least the variability of those runs that he had data for -- to take that into account when setting the limit.

And therefore, I do believe that this unit does appear to me to establish the maximum achievable control technology floor for this source category, and therefore I will support this amendment.

Do other members have -- other members here have comments before I ask John?

John, did you have any questions or comments that you wanted to add to this?

MR. HANSON: No, I don't. I agree with what has been said.

MR. LANGFORD: Thank you.

Any other comments from board members?
If not, I'll ask for the vote again.
I'll again start on my left.
Mr. Moore?
MR. MOORE: Aye.
MS. THOMSON: Thomson, Aye.
MR. BUCKHEIT: Buckheit, aye.
MR. LANGFORD: Langford votes aye.
MR. HANSON: Aye.
MR. LANGFORD: And Mr. Hanson voted aye.
So it is also a five to zero vote for changing those limits.
Was there any need for us to repeat those limits?
You got those? You guys got those?
MR. FEAGINS: Yes.
MR. LANGFORD: Are there other amendments that the members would like to propose?
THE REPORTER: If I may -- I need about one minute to take care of something, if this would be a good time.
MR. LANGFORD: She needs one minute, and I need a minute as well.
I am going to take a five-minute stretch break, because I think I can get there and back

by then.

(Whereupon, a short recess was taken.)

MR. LANGFORD: I call this meeting back to order after our brief recess.

Still under deliberation is the consideration of the permit for the Dominion Virginia City Hybrid Energy Center.

Do we have -- this is a poor question -- do we have additional amendments that want to be proposed?

MR. MOORE: I have two.

MR. LANGFORD: One at a time.

MR. MOORE: I will.

The first -- and this relates to the use of biomass.

I would move that we add the following: Use of biomass -- now these -- and what Dominion gave us is Number 22 and 23, but they would just be appropriately numbered in a section.

The first paragraph is entitled, "Heat Input."

After the first 36 months of commercial operation, the company will agree to use at least 5 percent biomass. Starting in the fifth

year of commercial operation, the company agrees to increase the use of biomass by an additional one percent per year up to a maximum of 10 percent. For purposes of such biomass requirement, percents shall be determined by the total biomass heat input for any given year divided by the total heat input for any given year, averaged over a rolling three years.

Second paragraph: Should market conditions indicate that biomass fuel has a significant rate payer impact or promotes tree cutting, such biomass requirement shall be reduced or eliminated until market conditions correct.

Dominion shall retain an independent consultant to inquire into such matters and obtain approval of the elimination or reduction of the practice from the Department of Environmental Quality.

MR. LANGFORD: Is there a second?

MS. THOMSON: Second.

MR. LANGFORD: There is a motion and a second.

Is there discussion on the motion?

MR. JOSEPHSON: Mr. Chairman, may I be

heard?

MR. LANGFORD: Yes.

MR. JOSEPHSON: Just for purposes of clarification, what you read was the language that Dominion agreed to based on what the -- conditioned upon what the final permit plan looked like.

MR. MOORE: That is correct.

MR. JOSEPHSON: What you are moving at this point is the agreement of Dominion to do this --

MR. MOORE: No.

MR. JOSEPHSON: You may want to change that language into more direction terms as opposed to "based on the company's agreement."

MR. MOORE: I didn't -- the language is what they proposed but I want to use this language.

MR. LANGFORD: Mr. Josephson -- the first paragraph -- look at the end of the first paragraph, they wrote the words "will agree to" and Mr. Josephson is suggesting that is not an appropriate motion language?

MR. JOSEPHSON: It is not regular.

MR. LANGFORD: The first line of the

first paragraph at the very end?

MR. MOORE: Oh, I'm sorry. I'm sorry.

MR. LANGFORD: At the end of 36 months commercial operation -- the company -- excuse me, Mr. Moore.

MR. MOORE: I'm sorry.

MR. LANGFORD: Mr. Josephson, I am asking if there was only that one place that you had noted that discrepancy?

MR. JOSEPHSON: Yes.

MR. LANGFORD: I think there is another occasion of "agrees," which we need to strike in the third line.

MR. MOORE: I am sorry. I thought that was --

MR. LANGFORD: Obviously, the company wrote it, and it certainly is -- their agreement would be contingent upon the things they stated earlier.

MR. JOSEPHSON: Mr. Chairman?

MR. LANGFORD: Yes, sir.

MR. JOSEPHSON: I really didn't pay that much attention to the reading of paragraph 23, but I thought that there was some discussion about that, that that includes some sort of

condition.

MR. LANGFORD: There's additional language. That has been corrected from the discussion in here.

I believe the two places where there's -- company agreement is implied or stated is that first line -- the first paragraph in the third line.

MR. MOORE: It would now read --

MR. LANGFORD: If you could just restate --

MR. MOORE: After the first 36 months of commercial operations, company shall use at least 5 percent biomass.

Starting in the fifth year of commercial operation, the company shall increase the use of biomass by an additional 1 percent per year up to a maximum of 10 percent. For purposes of such biomass requirement, the percent shall be determined by the total biomass heat input for any given year, divided by the total heat input for any given year, averaged over a rolling three years.

MR. LANGFORD: And the second one -- go ahead and read it so that there is a

clarification.

MR. MOORE: Should market conditions indicate that biomass fuel has a significant rate payer impact, or promotes tree cutting, such biomass requirements shall be reduced or eliminated until market conditions correct. Dominion shall retain an independent consultant to advise with such matters and shall obtain approval for the elimination or reduction of the practice from the Department of Environment Quality.

And I would leave it to the DEQ if there's further words that need to be done, but basically Dominion will hire an outside person who will come in and tell them whether they need to reduce or eliminate, and then they will go to DEQ and DEQ's approval will have to be --

MR. LANGFORD: Ms. Thomson, do you continue to second the motion?

MS. THOMSON: I do.

MR. LANGFORD: She does.

MR. LANGFORD: There is a motion and a second.

I'll start the discussion.

As has been noted here, this is a

language that was offered conditional by the company, on the current draft permit at their agreement. And it is noted here that they do not necessarily agree with it at the current time or may not in the future, given where we may wind up with the permit.

Is there other discussion on this motion, Mr. Moore?

MR. MOORE: I think it is important -- if we have this facility, it is important that if it is a hybrid plant and biomass removal is going to be used, we need to insure that it is used.

It is certainly a reasonable ramp-up period that they would not even have to use any of it -- I certainly hope they would -- for the first 36 months, but it would be after that they would use at least 5 percent and then ramp up 1 percent per year for a maximum of ten percent.

So we're talking about -- I guess that's 20/20, when they'll be at 10 percent.

I also think it is appropriate that it be done on -- based on the percent of input. The company should also be able to stop or reduce

using biomass if, in fact, market conditions are such that it would have rate payer impact in Virginia -- or rate payer impact or promote tree cutting. And I think what is provided is they would hire an outside consultant and get their report and come to DEQ, and have to have DEQ's approval.

But I think that is appropriate and I think that will protect the company.

MR. LANGFORD: Mr. Buckheit, did you have a comment?

MR. BUCKHEIT: Yes. I recognize that DEQ -- Dominion proposed this voluntarily. I think we have the authority that if we chose to, we could require it, under the Virginia Statute -- not the federal law -- it is clearly consistent with Virginia Energy policy and with all of what has occurred over the past several years under the Governor's energy plan.

I understand that Dominion -- if they don't like the other parts of this permit, that they can challenge the entire permit including this condition, but I don't think we can sit here and sort of bargain. So we have to put it in or not put it in.

So I would support putting it in, but I recognize that Dominion is free to challenge it.

MR. LANGFORD: Ms. Thomson, do you have comment on anything you want to say on the amendment?

MS. THOMSON: Not at this moment, but I might change that in a few minutes.

Please go ahead.

MR. LANGFORD: I acknowledge everything Mr. Burkheit said and agree with that.

It appears to me that the use of the biomass will help in the S02 removal rates, that is because biomass has essentially no sulfur in it to speak of, and therefore to the extent that they can burn the biomass fuel, they have less sulfur going in and presumably less sulfur coming out.

So it certainly is -- I don't view this as something that is a hindrance to them, given their stated goals in their presentations for this unit.

I agree that with Mr. Burkheit that they had agreed to do this under certain other circumstances, and I am comfortable in going

ahead and putting the language in this permit and to see where that whole permit may fall.

Mr. Hanson, did you have anything you want to say about it?

MR. HANSON: No, I don't.

MR. LANGFORD: And did you change your mind, Ms. Thomson?

MR. MOORE: Let me just -- if I may, just one second.

I of course acknowledge that Dominion may not agree with what we have done and I did not seem to want to imply that they were still for this. They may or may not be.

The point is, we need to have something in this permit that deals with this. This does it, and I think it is fair to the company and fair to the citizens of the Commonwealth.

MS. THOMSON: I just did want to add one comment, and that is under the conventional way of calculating greenhouse gas emissions and these conventions are decided upon by the scientists around the world, the IPCC is the signal organization on wood waste -- is considered biogenetic carbon, which is part of the natural carbon balance. That does not add

to atmospheric concentration of C02.

So to the extent that biomass is burned here, under the IPCC's way of calculating things, that would in fact avert carbon emissions at this facility because of sequestration.

MR. LANGFORD: I won't quibble that carbon emissions is going to be there, but they won't be counted.

MS. THOMSON: It is mitigated by biological sequestration.

MR. LANGFORD: Are there other questions or comments on this?

If not, I'll call the vote.

Mr. Moore?

MR. MOORE: Aye.

MR. LANGFORD: Ms. Thomson?

MS. THOMSON: Thomson, aye.

MR. BUCKHEIT: Buckheit, aye.

MR. LANGFORD: Mr. Buckheit voted aye.

MR. Langford votes aye.

Mr. Hanson?

MR. HANSON: Aye.

MR. LANGFORD: Aye. Okay.

Then that one is approved by zero.

There is another amendment -- at least one more -- there is several more actually, but Mr. Moore would you like to put another amendment?

MR. MOORE: Yes. This is the one that deals with the gob piles that you asked me to defer when I made my first motion regarding S02 emissions.

And this would go in an appropriate place.

In the event the permittee desires to burn waste coal, it shall present a plan to the DEQ for approval, detailing the proposed pile or piles to be burned.

The DEQ may approve, reject or amend the plan, including requiring the permittee to burn or remove and store safely all coal from one or more piles.

The DEQ shall not require through this approval process the use of more biomass than would otherwise be required in the facility.

MR. LANGFORD: More biomass -- is that what you meant?

MR. MOORE: I'm sorry. More waste.

MR. LANGFORD: Waste coal.

MR. MOORE: More waste coal than would otherwise be burned in the facility -- I've got "waste coal" here.

MS. THOMSON: I'm sorry. Could you just repeat that again?

MR. MOORE: In the event the permittee desires to burn waste coal, it shall present a plan to DEQ for approval, detailing the proposed pile or piles to be burned.

The DEQ may approve, reject or amend the plan, including requiring the permittee to burn or remove and store safely all coal from one or more piles.

The DEQ shall not require through this approval process the use of more waste coal than would otherwise be burned in the facility.

MR. LANGFORD: Now, we have the motion.

Do we have a second?

MS. THOMSON: Second.

MR. LANGFORD: Ms. Thomson seconds.

MR. MOORE: I would leave open for the staff, if I may do this properly -- I do not have language there to protect the company in their negotiations with the gob pile owners, and we certainly do not want to interfere with

that. So to the extent it needs to be secret, and they are not able to negotiate and cut the deal and then file a plan -- if that's the case, then I think it doesn't matter because they have their deal.

But if it creates a problem and they need secrecy before that, I want to insure that the company has that.

MR. LANGFORD: Is there other discussion by board members about this amendment?

MR. PAYLOR: Mr. Chairman, may I just make a clarifying question?

So the motion includes the recognition that the staff may need to make some amendments to that to assure those concerns?

MR. MOORE: Yes, confidentiality concerns to protect the company in their negotiating.

MR. LANGFORD: I would make a comment about this amendment.

I am less comfortable -- in fact, I am not comfortable with this amendment. It differs to me from the biomass amendment because this isn't requiring so much coal or not. It is not really dealing with fuel to the plant as much at it is, in my view, dabbling in

the areas that are best left to Mines Minerals and Energy or the Waste Management board to deal with those plans.

And as such, I guess I'm not comfortable requiring this plan, because it just -- it doesn't even have a close relation to the actual air permit that we're dealing with.

So for that reason I intend to vote against it.

Do the others have a comment they want to --

MR. BUCKHEIT: Actually, I would propose an amendment to the amendment, which is rather -- and I just talked to Mr. Paylor and he agrees -- that it is Mines, Minerals and Energy who should be looking at it.

MR. LANGFORD: Okay.

MR. BUCKHEIT: It is their bailiwick. They are the experts.

MR. LANGFORD: Can we say that they shall file something there --

MR. BUCKHEIT: Yes. As opposed to the DEQ.

MR. LANGFORD: We will do this correctly. We have a motion to amend the amendment.

Do we have a second for the amendment?
MS. THOMSON: I'll second.
MR. LANGFORD: And you second it. Okay.
Let's have discussion on the amendment to change from DEQ to DMM -- or MME.
MR. PAYLOR: The point that I was making to Mr. Buckheit is in fact that DMME would be the agency that we would turn to to decide things about priorities and that sort of thing.
I am a little bit less sure and haven't had a chance to think about exactly how we would assure confidentiality when we bring another agency into that discussion.
MR. BUCKHEIT: Aren't they subject to the same confidentialities as all agencies in Virginia?
MR. PAYLOR: Not necessarily because you have got separate statutes under the air pollution control.
For example, when you are requiring information of a company -- that may not be the case with DMME.
MR. BUCKHEIT: I think DMME is here.
Can you help us out?
MR. LANGFORD: I'm not sure --

MR. MOORE: Let me suggest this, that it probably isn't something we can do on the fly.

Why don't we add to this motion that in preparing this provision, the staff will consult -- Mr. Paylor, if you can see if this is all right -- that the staff would consult with the Department of Mines and Minerals and work together on language that would both require that they make the application having control by them and to the extent possible, protect the company as far as their confidentiality in the negotiating process.

Is that doable?

MR. PAYLOR: Well, we certainly would consult with them -- and I am beginning to lose track of exactly how this would all go together.

Another option, rather than the amendment that Mr. Buckheit suggested, might be just to say "DEQ in consultation with DMME," and leave DEQ as the controlling party.

MR. MOORE: That is fine with me.

MR. LANGFORD: Well, we need an amendment to the amendment to the amendment to do that.

MR. MOORE: Will it help you?

MR. LANGFORD: No. It won't. It won't help me. I believe this is not something that should be in the air permit.

But I am supporting it within Mines, Minerals and Energy instead of DEQ. To that extent, I support your amendment to the amendment, but I intend to vote against the amendment.

MR. BUCKHEIT: I move to amend my amendment.

Am I allowed?

MR. LANGFORD: Sir?

MR. BUCKHEIT: I move to amend my amendment such that the --

MR. LANGFORD: You can withdraw your amendment.

MR. BUCKHEIT: I withdraw it and substitute.

MR. LANGFORD: Okay.

MR. BUCKHEIT: An amendment to the effect that the consultation -- if I understand Mr. Moore's amendment, shall be DEQ, comma, in consultation with Mines, Minerals and Energy.

MR. MOORE: I second the amendment.

MR. LANGFORD: And you seconded that.

MR. MOORE: Yes.
MR. LANGFORD: Any other discussion on this particular issue?
I will say that I still don't feel comfortable putting this kind of a requirement in the air permit. I am perfectly happy to have them do it. I think it gives the public some assurance that one of the reasons for building the hybrid energy center will, in fact, take place -- that it will burn some waste piles, but I am not comfortable in putting that in there, so I still intend to vote against it.
And having said that, the amendment to the amendment -- okay -- so let's have a vote on the amendment to change it to a consultation with DMME.
All in favor?
MR. BUCKHEIT: Aye.
MS. THOMSON: Aye.
MR. LANGFORD: Aye.
MR. MOORE: Aye.
MR. LANGFORD: John, did you have an opinion on changing it to DMME?
MR. HANSON: Aye.

MR. LANGFORD: Okay. So it is unanimous.

And now we will vote -- unless there is other discussion on the amendment, we will vote on the amendment to add a requirement in the air permit to prepare a plan and that is now in the DEQ in consultation with DMME regarding the conditions in which the waste coal piles are selected and used.

Any further discussion on that?

MR. BUCKHEIT: Just one thought, in hopes of persuading you to join us.

The standard purpose for allowing non-commercial coals -- gob piles, et cetera, was in fact, cleaning up existing gob piles.

We have the authority to restrict -- under the Clean Air Act, to restrict Dominion to burning .9 percent 12,000 BTU coal, et cetera.

We elected not to do that. For me, it was a recognition that there was positive environmental benefit to cleaning up these gob piles, coupled with the recognition that the controls that Dominion was suggesting were at very good levels.

I think it has to be said that

nonetheless, burning gob piles and waste piles would probably have greater emissions then if you burn waste coal piles. You know, in our tour with the Department of Mines and Minerals, they showed us some particular gob piles that were of particular environmental concern.

I think that it is within our authority and certainly consistent with common sense, and Dominion agrees, to say: Well, if we are going to sort of take into consideration that they say the purpose of this program is to clean up waste piles, that at least there be some ability of some part of the government to say: Well, let's go after the most environmentally sensitive ones first.

And that's what this amendment is about.

MR. MOORE: It is also about insuring that if the company chooses to burn waste coal that if it starts on a pile -- I think -- let me back up.

As I said, just taken independently, obviously burning the waste coal rather than cleaner coal puts more air emissions.

But if they get -- and they certainly should get the removal efficiencies up high

enough to where they can meet the .022 limit, that sets on a clean coal basis, if they can burn this coal, that is good, but we don't want -- at least, I want to make sure some regulatory body is looking at this, and if it is appropriate, saying to them: You can't take half of this pile and disturb that one, and then move on and pick a little more from another pile -- that if the right way to do it is start on a pile and go through and finish that pile and clean that one up, that there will be an agency to do that.

And when they do it, Mr. Buckheit said they start with at least one of the -- one of the piles that presents the greatest problems.

MR. LANGFORD: Thank you for your clarification, and those reasons you articulated are exactly the reasons why I do not believe this belongs in the air permit.

It belongs, if nothing else, in somebody's waste permit, or somewhere else. So I continue to oppose it.

But we will vote and see where it goes, if Ms. Thomson wants to comment.

Would you like to vote?

MR. BUCKHEIT: I vote aye.
MS. THOMSON: Thomson votes aye.
MR. BUCKHEIT: Buckheit, aye.
MR. LANGFORD: Langford votes no on this matter.
John?
MR. HANSON: Hanson votes no for the reasons expressed by Mr. Langford.
MR. LANGFORD: Okay. So the motion passes on a three to two vote. So the language that was read and was proposed will be inserted into the PSD permit, I would assume.
Correct? It goes into the PSD permit.
Okay. Are there other amendments?
MS. THOMSON: Yes.
Dominion has for some months and up to today's meeting -- volunteered, if this permit is issued, to convert the Bremo Bluff facility, somewhat after Virginia City goes online, so I would like to introduce an amendment that essentially puts this condition to that Hybrid City Energy Center permit.
It is simply that Dominion will convert the Bremo Bluff power plant to natural gas within two years of commencement of operation

at the Virginia Hybrid Energy Center.

MR. LANGFORD: Is there a second?

MR. MOORE: I'll second.

MR. LANGFORD: Mr. Moore seconds that. Is there discussion on this?

MS. THOMSON: Yes.

I guess there has been a lot of concern over the prospective carbon dioxide emissions from the hybrid energy center, so I would like to talk about that a little bit in connection with this amendment which involves voluntary reductions -- and I stress "voluntary reductions," not only of carbon dioxide -- obviously of other pollutants as well.

Dominion has estimated that the hybrid energy center facility will emit 5.3 million tons of carbon dioxide annually.

For perspective, according to the scientists I consulted to balance these carbon dioxide emissions through biological sequestration, a fancy term for planting trees, we would need to plant and maintain 3600 to 4900 square kilometers of pine trees.

The upper end of that range corresponds to 5 percent of Virginia's area.

For more perspective, in estimates presented to Governor Kaine's Commission on Climate Change, DEQ showed that Virginia's 2005 greenhouse gas emissions totalled 175 million tons a year.

We have heard again and again in hearings and in written comments that the board should require specific technological solutions such as IGCC to insure that the projected greenhouse gas emissions from this facility are controlled.

The air board today embraces, and adopts in the permits, voluntary greenhouses gas reductions that will come, first of all, from the use of biomass. We have had that amendment already. Also in the form of the Bremo Bluff conversion.

By adopting the voluntary steps into this permit, we consider the following facts:

Carbon dioxide is a pollutant under the Clean Air Act. However, there is as yet no regulatory framework for carbon dioxide or greenhouse gas emissions under the Clean Air Act, specifically under the provisions we are looking at here today.

And in addition to our generalized concerns as board members, Governor Kaine has indicated in many contexts, his efforts to reduce greenhouse gas emissions in Virginia and elsewhere.

For example -- I won't belabor the many ways in which Governor Kaine has indicated his support of this action to reduce greenhouse gases. He has endorsed the Warner-Lieberman bill. He signed the April 2008 Governor's Declaration on Climate Change. He, of course has formed the Commission on Climate Change, and he has set a greenhouse gas emission reduction goal for Virginia.

But his support is certainly in keeping with the 17-odd states in the United States that have come forth on their own to reduce greenhouse gas emissions in lieu of action at the national level.

I stress today that the actions we are taking is limited to this applicant, based on their voluntary reductions. We are doing this to take care of what would otherwise be substantial uncontrolled emissions of a Clean Air Act pollutant. The step is specific to

this application and this setting, based on representations made by this applicant.

The exact emissions averted that we will get in these two combined actions are a little in question. It depends on specifics with regard to both facilities, but I think it is safe to say that these carbon dioxides savings would be at least in the hundreds of thousands of tons a year, if not perhaps more.

MR. LANGFORD: Are there other comments on this motion?

MR. BUCKHEIT: Yes.

There is absolutely no suggestion that this board has the authority to require Dominion to repower Bremo Natural Gas through this permit or otherwise.

Dominion has offered to do that. That is part of the package representing its commitment to the community. This permit is a reasonable vehicle, probably the only vehicle -- certainly the only vehicle the public has confidence in, in which to accept Dominion's offer.

And so I think it is not inappropriate to include this in the air permit.

I think there's an additional suggestion

that has been made by some, that, well, Dominion is going to do it anyhow, so what's the big deal?

As I pointed out yesterday, I think with the issues up in the air and lots of other things floating around, I would be for taking that offer while it is still available.

Oftentimes, companies' plans change. They are willing now to make it, and so I am willing to accept it.

MR. LANGFORD: Mr. Moore?

MR. MOORE: The offer has been made through Mr. Buckheit, what he said.

I would also note that the offer that was presented to us -- we didn't discuss C02, I don't believe. But in their presentation to us today, in a separate page on this as the Bremo proposal, and it outlines, the S02, the NOx and the mercury reductions.

So independent of C02, it is very appropriate that we do this, and include it in this permit.

MR. LANGFORD: My understanding is that it has been offered by the applicant, and I believe there are some advantages, probably, to

having it in some sort of regulatory framework as Mr. Buckheit alluded to, so while I also agree, it is not something that we have the authority to require, my understanding is that this is something that the company may actually want to have codified in some way.

It would give them something to point to. So I am okay with this amendment.

Are there any other comments?

John, you can just jump in any time you have a comment. I'll interrupt, if you have any.

MR. HANSON: I would interrupt, but I don't have one.

MR. LANGFORD: All right. Are we ready to vote?

We will start at that end.

MR. MOORE: Moore, aye.

MS. THOMSON: Thomson, aye.

MR. BUCKHEIT: Buckheit, aye.

MR. LANGFORD: Langford is aye.

MR. HANSON: Aye.

MR. LANGFORD: And Hanson votes aye.

And that one is passed.

The next amendment is --

MR. BUCKHEIT: I have an amendment with respect to the C0 limit for the MACT permit.

MR. LANGFORD: Okay. We are talking about the MACT permit and the carbon dioxide limit.

Would you make your motion, Mr. Buckheit?

MR. BUCKHEIT: Yes. I believe the limit proposed by staff, as the staff is making its presentation, was greater than the emission limitation -- the emission limit for another facility.

Is that correct, Mr. Dowd?

MR. DOWD: Yes, Mr. Buckheit.

MR. BUCKHEIT: And what is the emission limit for the other facility?

MR. DOWD: I believe it was .01.

MR. BUCKHEIT: And I think your concern, as expressed by the staff, was the NOx C0 tradeoff?

MR. DOWD: Yes, sir.

MR. BUCKHEIT: Yeah. I just don't find a place for that in the statute. I am concerned that --

MR. FEAGINS: Mr. Buckheit, I heard just a moment ago it was .01.

MR. BUCKHEIT: Tell me about it.
MR. DOWD: It is .1.
MR. MOORE: The limit is .15.
MR. BUCKHEIT: The upper limit is .10. Is that correct?
MR. DOWD: That's correct.
MR. BUCKHEIT: Again, I'm concerned that unless there is a real feasibility question that major concern that this unit can't meet this, we are opening this thing up to an easy hit on a lawsuit for failure to set the MACT limit at the lowest achievable limit, and I guess -- push me back one more time, staff, before I make my motion.
MR. LANGFORD: While they are pushing back, just for clarification -- which unit had the actual .1?
MR. DOWD: It was Seward.
MR. LANGFORD: That was Seward.
MR. DOWD: Seward. Staff stands by its initial recommendation, understanding.
MR. BUCKHEIT: There's no new arguments. That's all.
I move that we reduce the limit to .10 pounds per million BTU.

MS. THOMSON: Second.
MR. LANGFORD: We have a motion and a second to reduce the permit limit on carbon monoxide from 0.15 to 0.10 -- 0.10.
And my notes here show that that actually is AES Puerto Rico rather than Seward.
I am looking back at the presentation and it shows that the --
MR. BUCKHEIT: Right.
MR. LANGFORD: The Virginia City listed at .15, as stringent -- Seward is .15 and Puerto Rico is .10.
Am I correct?
It is on page 25 of your MACT presentation.
MR. DOWD: What was the question, Mr. Langford?
MR. LANGFORD: I was just trying to get clarification as to which unit actually had the achievable technology.
At one point I thought I heard it was Seward, but it appears to be the Puerto Rico unit at .10.
MR. DOWD: Well, Puerto Rico is .10.
MR. LANGFORD: And Seward was --

MR. DOWD: Seward was .15 and three pounds -- I'm sorry, a three-hour average.

MR. LANGFORD: Three-hour average.

Okay. So I just -- with that clarification, is there a motion?

MR. BUCKHEIT: Hold on a second.

That's an eight-hour average?

MR. DOWD: The one in the permit is an eight-hour average.

MR. BUCKHEIT: AES is an eight hour? What is ours?

MR. DOWD: 30-day rolling average.

MR. BUCKHEIT: All right. So I'll stick with .100 30-day rolling average.

MR. LANGFORD: We have a motion and a second, I think.

MS. THOMSON: Yes, we do.

MR. LANGFORD: To change the C0 limit from .15 to .10 in the MACT permit.

.100? You're adding an extra decimal beyond what is in there. I believe the others are .10.

Do we have discussion on this motion?

MR. JOSEPHSON: Mr. Chairman, may I be heard?

MR. LANGFORD: You may.
MR. JOSEPHSON: What is the time period that you are ruling your .10?
MR. BUCKHEIT: I am staying with 30-day rolling.
MR. LANGFORD: Yeah. I believe he indicated he was going to stay with the same 30-day rolling average, which, if we are ready to start discussion on this, is actually a little less stringent than the eight hour.
Correct?
MR. BUCKHEIT: Correct. I am not trying to drive Dominion's numbers down arbitrarily. I am trying to get to a number that we can defend in court.
And, you know, so maybe it should be one zero zero -- one zero on an eight-hour average. I think we'll take our chances.
MR. LANGFORD: I think we have got to have the right limit whether it is -- other comment on this one?
While I am still talking, I'll just go ahead and -- again, like my previous comments for Maximum Achievable Control Technology which this limit is, we are required to consider as

the floor, the best performing similar unit and it does appear that the AES Puerto Rico unit has performed at better than the Seward and therefore would be the MACT floor for this, and therefore I think that a 0.10 is an appropriate change.

Other comments?

Seeing none, we will call the vote.

MR. MOORE: Moore, aye.

MS. THOMSON: Thomson, aye.

MR. LANGFORD: Are you voting?

MR. BUCKHEIT: Aye.

MR. LANGFORD: Buckheit votes aye.

Langford votes aye.

Mr. Hanson?

MR. HANSON: Aye.

MR. LANGFORD: Okay. Five zero on CO.

Next is -- are we out, or do we have more?

MR. BUCKHEIT: I would like to move the board to consider whether to remove Condition 33, relating to stack tests.

MR. LANGFORD: I'm sorry. I am not sure I understand what that means to consider removing --

MR. BUCKHEIT: I want to get some discussion. I would like to have some discussion about this. I am not convinced, and if I am wrong, I will withdraw it.

THE REPORTER: I can't hear you.

MR. BUCKHEIT: I would like some discussion.

MR. LANGFORD: Go ahead and make the motion and then we will bring the discussion and then we will either say yes or no.

Well, moving to considering -- make a motion to put it in.

MR. BUCKHEIT: All right. I have been beaten up by my chairman. He is forcing me to move to remove Section 33.

MR. LANGFORD: You do not have to vote for your own motion.

MR. BUCKHEIT: I understand. I may vote against my motion.

MR. LANGFORD: And is there a second?

MS. THOMSON: I second.

MR. LANGFORD: Okay. We have got a motion and a second.

For John's benefit -- I don't know -- you probably have your permit there. This provison

we're talking about is in the MACT permit, which is in Tab E, and it is Condition 33.

MS. THOMSON: It is 19.

MR. LANGFORD: It is page 19. It is the MACT permit.

Somebody took it out of my book. That is why I didn't have it.

It is on page 19. It is provision -- Paragraph 33, it is what we heard yesterday referred to as the "out clause."

And it goes into something -- I won't read the whole thing because it is several paragraphs long, but it essentially goes into the -- it says there at the bottom, there is uncertainty at these low levels, and in order to obtain an adjustment, there is a provision set forth that if the permittee is unable to achieve the limit that is in the permit that they can apply for, and perhaps receive, if approved, a modification of that permit.

And I think we had some clarification earlier that that would still be subject to public comment and so forth.

It changed to whatever was really achievable.

And this is the so-called "out clause" that we heard some from yesterday.

And I think you found it -- right, John?

MR. HANSON: Yes, I did.

MR. LANGFORD: We're having a discussion on the motion.

MR. MOORE: I just want to confirm that -- two things: Number one, if this happens, is this handled in essence like this permit -- it has got to be noticed, opportunity.

Can the staff -- Mr. Dowd, can you --

MR. DOWD: Yes, Mr. Moore.

They would come to us basically with a new permit application, claim that they could not -- that the best controlled similar source -- we did not get that right with respect to what they actually demonstrated.

MR. MOORE: Or at least that they could not achieve it?

MR. DOWD: That's correct.

MR. BUCKHEIT: Or at least that it is unfeasible for them. It is not that we got -- at the time they challenge the permit, they will have that and they will go through that permit. This is later -- five years from now

-- long after the permit, if they come back and they say: We built it. We did the best we could, but we couldn't get there.

Correct?

MR. DOWD: Well, hopefully they would come to us with that long before five years.

MR. BUCKHEIT: Because they haven't built it in four years.

MR. DOWD: All right. Five years from when they started.

MR. BUCKHEIT: Right now is when this trick thing might be offered.

Four years of construction, one year after running. So this is not the challenge to the permit that we get the BACT level wrong.

And let me speak to this and maybe -- don't go away.

This is comfort language.

MR. DOWD: This is what? Excuse me?

MR. BUCKHEIT: Comfort language. The law allows this.

Correct?

MR. DOWD: I believe it does, Mr. Buckheit.

MR. BUCKHEIT: Whether or not it is in

the permit, it allows it.

MR. DOWD: I believe it does.

MR. BUCKHEIT: And the reason I raise it for discussion, is quite frankly, the environmental groups have singled this out as an escape hatch.

And sitting in proximity in a MACT permit, where the feasibility of the source is not allowed to be considered, it is the floor anyhow -- I am afraid that it could be read as something like what the environmental groups are asserting -- that we are not really setting a .09 pounds per trillion BTU mercury limit, seeing that there is this escape hatch.

And while I understand it might be comforting to the company to have this here, it is as simply optics, in that it doesn't change underlying Virginia law.

Isn't that correct, Mr. Dowd?

MR. DOWD: I think basically that is correct.

I do want to add that the Pennsylvania permits do contain a provision very similar to it.

MR. BUCKHEIT: Normally, this is a good

thing. I am not objecting to this kind of approach.

This is -- my idea of permitting is you set a tough limit, the company goes out and does its best to meet it, and if it can't, we don't shut them down in America. We don't shut them down anywhere. We work it out.

And there is a mechanism and it is a public process to do that.

The only reason I raised this, is because it was featured significantly in the criticism of the MACT permit, and it seems to serve no purposes other than to act as a lightning rod.

And I raise it for discussion.

MR. LANGFORD: It is on the table for discussion.

MR. BUCKHEIT: And again, I reserve the right to vote against my own motion.

MR. MOORE: Let me ask another question, if I may.

If they come in and say: You know, we are trying and we can't do it.

The other suggestion was: Well, you know, in the meantime, we look back at the BACT permit, which is 72 pounds.

Is there -- I mean, should we take out the 72 pounds?

Why do we -- I am just -- can they make that argument successfully in your view?

MS. THOMSON: I'm not quite sure what type of argument you mean.

MR. BUCKHEIT: I thought we were not setting a BACT limit for mercury.

Did I miss that?

MR. FEAGINS: We are not establishing the limit of the PSD permit for mercury on the basis of BACT.

The limit originally proposed in the first draft and in the most recent draft is remaining -- the proposed PSD permit unchanged.

MR. BUCKHEIT: Why is it in the PSD permit? Why is it in there at all?

Why don't we just knock it out?

MR. FEAGINS: To remove the permit, we believe would be -- to remove the limit from the permit, we believe would be a relaxation of the permit, and would require --

MR. BUCKHEIT: You don't have --

MR. FEAGINS: And would require returning to public participation in its full intensity.

MR. MOORE: What about if we changed it to what is in the MACT permit?
MS. THOMSON: Yes.
MR. MOORE: I mean, if the MACT permit is the only thing that's binding, then let's make sure that it's the only thing that is binding.
MR. FEAGINS: Our intention was to retain the 72-pound-per-hour limit in the PSD permit as a backstop, in the event that something --
MR. BUCKHEIT: But it is not a PSD --
MR. LANGFORD: Let him finish. Wait a minute. Let him finish. Let him finish.
MR. FEAGINS: In the event that something happened to the MACT permit, we would have a backstop.
MR. MOORE: I am sorry. If something happened to what?
MR. FEAGINS: The MACT permit.
MR. MOORE: Well, if we are looking at that, 72 pounds is not a backstop.
I mean, 72 pounds --
MR. FEAGINS: It was a MACT limit established as part of the PSD permit.
MR. MOORE: Well, I understand and I think the only reason it wasn't drastically

reduced is under BACT -- I am not talking about -- you know, I'm not satisfied with the 72 on the BACT.

MR. BUCKHEIT: We didn't revisit --

MR. FEAGINS: In my discussion this morning, I said -- or I intended to say, if I didn't, that we were very careful to remove the citations that referred to it as a BACT pollutant, and we just cite general authority, that we want to retain that limit.

MR. BUCKHEIT: That is under Virginia law, not federal law.

MR. FEAGINS: We believe that it is, yes.

MR. MOORE: Why can't we change it to make the MACT limit?

MR. BUCKHEIT: Under general authority.

MR. FEAGINS: You're the board. I suppose you could.

Well, the argument against it is that you're taking -- you would have to not only take that out, you would have to take out a lot of the other language you would have to follow that, because that is not just a number in and by itself. I mean, there is a lot of other stuff that goes into the MACT permit.

MR. MOORE: Well, can we put the language in simply by note, incorporate by reference the MACT permit.

I am not comfortable at all with leaving something as a backstop that is 72 pounds.

MR. FEAGINS: Well, we did amend the draft permit to include a reference to the MACT permit, that said that the lowest limit established on an enforceable permit would prevail.

So it is connected to the MACT permit in --

MR. BUCKHEIT: Having done that --

MR. FEAGINS: Excuse me?

MR. BUCKHEIT: Having done that, don't you have your backstop?

MR. FEAGINS: In the event that the --

MR. BUCKHEIT: Okay.

MR. FEAGINS: That the MACT permit should go away.

MR. BUCKHEIT: So if we want to be protected, we report the 0.9 number over into the --

MR. LANGFORD: No. I don't think so.

MR. MOORE: Are you saying that if the

MACT permit gets struck down, then they could emit all the mercury they wanted and this would hold them down to 72 pounds a year?

MR. FEAGINS: That would essentially be correct, Mr. Moore.

MR. LANGFORD: Say that again, Mr. Moore.

MR. MOORE: That if the MACT permit got -- you know, was, you know, found not to be valid by the Court, then the company could emit what they wanted --

MR. FEAGINS: That can't be correct.

MR. BUCKHEIT: If this MACT permit were invalid, then they don't have any approval, and you would have to go through another process, reset another limit.

MR. FEAGINS: And until that time, it would be the backstop limitation for mercury.

MR. BUCKHEIT: But you're talking four years from operation. I mean, presumably everybody is delighted with this permit, and there won't be any challenges, but even if they are not, it will be over in two years.

MR. FEAGINS: Let me come back again.

It is -- what you're telling us -- and we would like Counsel's advice on this, that if

the MACT permit gets struck down, perhaps as not being stringent enough, they could emit what they -- and we did not have this provision, that the company could emit -- would not be limited in their mercury emissions?

MR. PAYLOR: I don't think it matters whether it is in the provision or not.

MR. BUCKHEIT: They can't operate without a MACT permit.

MR. MOORE: That's what I'm saying. If they can't operate without a MACT permit. If this one is stricken -- the one we adopt is stricken, then they don't have one and they can't operate.

MR. DOWD: Well, that would depend on what the court said when it struck it, Mr. Moore.

MR. MOORE: I'll take that risk, rather than approve something that a backstop is 72 pounds.

MR. BUCKHEIT: The suit on relaxing the 72 would come from the environmental groups -- not from the company.

MR. FEAGINS: I don't know where it would come from.

MR. BUCKHEIT: I think -- I'm willing to take the risk that we will get sued by the environmental groups if you take out the 72-pound limit.

MR. LANGFORD: I think we are mixing our discussion. We have a motion on Paragraph 33.

And let me try to put something in context and get my two cents in here, and then you can weigh in.

I believe that the concerns expressed by many people that this provision allows them to go to 72 is unfounded and unwarranted and isn't supported by the law or practice or policy in the department.

If they cannot meet the 8.1, they will be having --

MS. THOMSON: 4.5.

MR. LANGFORD: 4.5 Excuse me. Thank you.

If they cannot meet the very stringent mercury limit, they will have to make a demonstration to the department using their best ability to get the lowest numbers they can as to how they can get a number that's higher than the very stringent current limit.

And I just -- so it's not automatically that if they can't make the low limit they are automatically able to go as high as they want. That's just not the case.

MR. BUCKHEIT: I think we're mixing issues. And we'll come back with the 72 pounds.

Let's finish with the Provision 33 discussion.

MR. LANGFORD: On Provision 33, I agree with my colleague, and with staff from everything that I have heard -- the procedure outlined here is essentially the procedure that would be followed whether or not this provision is in the permit.

On the one hand, I am sensitive to the misunderstanding, in my view, of some of the public about what this provision means, because I believe that they think it allows more than in fact it really does. And while on the other hand, I am sensitive to the company that we have ratcheted down many of their permit limits, including this mercury limit, to very stringent levels, and this gives them at least some comfort that, as you say, in four or five

years, after 12 months of actual operation, that the staff will still know what those procedures are that they need to step through to try to alleviate the permit when, upon their best efforts, they -- and agreement by the department on their best efforts, that they are not able to achieve it.

So that is where I'm going kind of weighing between the two. And again, I'm a little bit on both sides, and I'll probably have some more to say.

Mr. Moore, did you want to talk about Paragraph 33?

MS. THOMSON: I guess I am sitting on the fence like the Chair.

To the extent that this doesn't really add anything to existing Virginia law, you have to say: Why is it there?

I guess I'm -- at this point, it is not compelling to me that we should take it out. I suppose I could be convinced the other way.

MR. MOORE: I would like -- if I may, I would like to ask Mr. Dowd -- I guess would be the appropriate person: Can I have your assurance that in essence this Paragraph 33

means nothing -- it adds nothing -- you know, that the company would be able to do exactly what is here if we didn't have this?

MR. DOWD: That is my understanding of Virginia law and regulations, Mr. Moore.

MR. MOORE: So if someone seeks to make the argument: My impression is they must have meant something by this, I gather we are at least making a record that we thought we were leaving in language that did not give anything in addition to what the law already did.

MR. BUCKHEIT: Let me offer a qualifier.

The pro is that it contains a list of things that must be demonstrated before the limit could be relaxed. And it is a comprehensive list. So it creates some structure for appropriate discussion.

The con is that it could be read to say that the department could raise the limit -- limits authorized by federal law.

If the MACT floor is the MACT floor is the MACT floor, and there is not a hardship exemption in the MACT process, we are now being explicit at the time that there might be a pending challenge, as opposed to letting the

system deal with it later on after the challenge period is over.

MR. LANGFORD: Mr. Moore?

MR. MOORE: I think that con is very important.

To the extent -- Mr. Buckheit, are you suggesting that while this language may be fine for Virginia law, in fact, currently under MACT, this wouldn't -- they couldn't do this?

MR. BUCKHEIT: Mr. Dowd, help me here. I think -- was it National Lime that says it doesn't have to be achievable by everybody?

MR. DOWD: I believe so.

MR. BUCKHEIT: One of those.

Okay. And so I believe that at a theoretic level -- and I really doubt that a federal court would wind up there. I think if it is not really achievable, the court would find its way around it.

But that's what the National Lime Court said.

And what we are saying here is: Well, if the floor isn't achievable -- this is five years from now -- and we are not revisiting what the board did -- then we are going to do

something, suggesting that we don't believe in National Lime.

MR. DOWD: It's a very stringent --

MR. BUCKHEIT: It is a push. I mean, first of all, it is a rather small issue, but it is also a push. I mean, I could flip a coin.

MR. MOORE: I'll make one more comment.

MR. LANGFORD: One more comment, Mr. Moore.

MR. MOORE: From what I've heard, I think we ought to take it out. I think it is not clear whether the law is precisely the same. It is not clear that this is what should be done under MACT, if -- assuming they can't achieve it. And I think we need to allow the law to stand as it is. I haven't heard anybody say that they are proposing to do anything any different.

And so, if we take it out, we haven't made a mistake.

If we leave it in, you know, it seems to me there's real room there to create a problem for us in the future.

MR. LANGFORD: Having heard the

discussion, and remembering our discussion about the uncertainty in the test methods for these amounts that are well below -- the emission limits are well below the applicability level for some of these tests at this time -- although, I have been reminded before that test methods get better with time, and we are talking about four or five years from now -- I come down on the other side of that fence.

I think, on balance, I think that I will vote to -- against the motion and vote to leave this condition in.

I agree with others -- from a legal standpoint I don't think it makes a whole lot of difference. I do think it gives some comfort to Dominion at a time when we have ratcheted down mercury limits with a test that is -- by some standards is -- will have a hard time measurng the limits that they are having to meet, so I'll come down on the other side of that fence.

Anybody else want to say anything before we vote?

MR. BUCKHEIT: I would like to see a head

nod from Dominion. The risks are both theirs.
MS. FAGGERT: Our preference would be to leave the condition in.
MR. LANGFORD: We will start this vote, and I'll start from the other side this time.
Mr. Buckheit.
MR. BUCKHEIT: Voting no on his own motion.
MR. LANGFORD: And the chair would vote no.
And Ms. Thomson?
MS. THOMSON: No.
MR. LANGFORD: Mr. Moore?
MR. MOORE: Well, the idea is that we all will be unanimous. I have grave concerns that we may come back -- well, someone may be -- somewhere -- it won't be us -- have to deal with this, but I am sympathetic to the company, and I will vote to leave it in.
So I vote no.
MR. LANGFORD: And Mr. Hanson?
MR. HANSON: No.
MR. LANGFORD: So there is zero yeahs and five nays. The motion is defeated.
Are there additional amendments?

Have we run out of amendments?

Mr. Buckheit are you anticipating coming back with an additional motion?

MR. BUCKHEIT: I'll let you know.

MR. LANGFORD: We are going to take a short intermission, folks, for about five minutes while some consultation takes place.

(Whereupon, a short recess was taken.)

MR. MOORE: Mr. Chair.

MR. LANGFORD: Mr. Moore.

MR. MOORE: When we accepted the Bremo proposal -- I forgot my former life, and we need to make that subject to the approval by the State Corporation Commission. They have to approve that.

Someone asked me, well, do you want to make it -- require them to file and require them to use their methods and this, that and the other?

And my answer to that is no.

They have offered to do this, and it is subject to commission approval and, you know, I think we just say that we accept their offer and it is subject to the commission approval.

MR. LANGFORD: There is a motion made.

Is there a second?
MR. BUCKHEIT: I second.
MR. LANGFORD: There is a motion and a second.
Is there any discussion on what Mr. Moore suggested?
I'll call for a voice vote on this.
All in favor say "aye."
MR. BUCKHEIT: Aye.
MR. MOORE: Aye.
MR. LANGFORD: Aye.
MS. THOMSON: Aye.
MR. HANSON: Aye.
MR. LANGFORD: All opposed say "no."
Since I didn't hear you then, John, I assume you voted "aye," or did you abstain?
MR. HANSON: I voted aye.
MR. LANGFORD: All right. That wasn't one of the two I told you about. That was an extra one.
Okay. Another motion?
MR. BUCKHEIT: I move to amend the MACT hydrogen chloride limit from .0066 pounds per million BTU to .0029 per million BTU.
MS. THOMSON: I second.

MR. LANGFORD: Would you like to explain your rationale while I look up the provision here?

MR. BUCKHEIT: Sure. This is in reference to our discussion earlier with Mr. Dowd.

The staff set the .0066 above the Spurlock and the oh oh two nine is some PC unit, in recognition of concerns about chlorine and mercury.

And I do accept and understand that chlorine content in the facility is essential to getting mercury to get something to a form that can be captured.

But as we discussed, offsetting limits, we can't make the tide not come in, we can't make the sun not go up and down. And the limit that we set will not affect the chemistry inside the boiler.

So, creating a higher ACl limit will not enhance mercury. The boiler will do what it does irrespective of what we do as permitting authorities.

I am concerned that if we do not reduce the limit to the .0029, which is the limit

achieved by what could be argued to be the best performing similar source, again, for no reason, we open the permit up to challenge and disruption.

I am quite comfortable that with this unit's extraordinary acid gas performance, that a .0029 limit is not going to be curtailing the activities at the source any more.

This is more by way of cleaning up the books to reduce litigation risk and make this permit as lawful as possible.

MR. LANGFORD: Mr. Buckheit, I understand the need to make sure we have the MACT standard here for HCl. I concur with your comments about the chemistry in the boiler.

I am however curious, because earlier we indicated that the similar source was the group of CFBs, and they have only generally referenced PCs for information.

And yet your motion appears to set the MACT floor at the performance of a pulverized coal boiler, not a circulating fluidized bed boiler.

Can you address your thoughts there?

MR. BUCKHEIT: Yes. I really -- I don't

think we want to open up this permit to arguments about what the definition of "best controlled similar source" is.

For mercury, for instance, I am convinced that it is the PC world is going to be chasing CFB world.

The PC -- the pulverized coal people are going to want to say they are not like the CFB world because CFB is so good.

When I made my statement, I said -- arguably with respect to the pulverized coal universe, there is about a 20 percent difference between the Spurlock unit and the Mid American unit.

Again, I think that the performance of this system is so much below anything that we are talking about here, that to create again just a litigation argument about whether we should have picked Mid America as opposed to whether we picked Spurlock, given where this unit is going to be -- I would -- again, it's a matter of making this the most defensible permit that we can without inviting extra arguments from the other side, especially where here the differences are small, and I think

well within the performance of the unit.

MR. LANGFORD: I hear what you're saying. I understand that there are two sides to this, and avoiding a risk from one may pose a risk from the other, in that we have previously defined "similar source" as CFBs and yet we are going below that without going through the lower MACT floor.

MR. BUCKHEIT: I don't think we actually defined -- I was careful not to define CFBs as similar source.

MR. LANGFORD: You may not have defined it, but I think the department has previously done that in their analysis of the permits. I don't know if it is in their presentation anywhere, but they told me that that's what it was.

MR. BUCKHEIT: There are probably a hundred things in the Department's response to comments that I don't agree with.

MR. LANGFORD: I understand you may not agree with it.

MR. BUCKHEIT: Okay. They don't have the authority. We have the authority.

MR. MOORE: Mr. Chairman, may I ask Mr.

Buckheit a question?

MR. LANGFORD: Yes.

MR. MOORE: I know that, you know, the floor is the floor is the floor. We can't consider the interaction of various pollutants and have one push down on one and push up another and have an impact on another.

At the same time, is this -- and the difference is less than 20 percent or about 20 percent -- is there an impact that -- will there be an impact on something else as a result -- I am not saying it is going from the 66 to the 29, but will there be an impact going from 35 to 29?

MR. BUCKHEIT: I don't think that any of these numbers will affect how the plant operates. I think the plant's acid gas performance is driven by S02 removal, and our selection of the .022 limit will drive how they operate the unit and these emission reductions will be sort of a co-benefit from the very extensive acid gas system that they have.

I don't believe that this will cause any change in operations of these units.

I think that all that I am looking at

here is getting a defensible permit.

MR. LANGFORD: I don't disagree that we are not talking about changes in technology or units, but to be consistent with my previous positions on other limits, I will have to vote no on the using of the Mid America Energy as the MACT limit, but I would vote yes on the Spurlock MACT limit with the double oh 35 rather than the double oh 29, for reasons I mentioned before.

Are there other comments on this or does anybody want to perhaps amend their motion?

John, do you have any comment?

MR. HANSON: I do not.

MR. LANGFORD: And hearing no other comment, I'll ask for the vote.

Mr. Moore?

MR. MOORE: I'll vote aye.

MS. THOMSON: Thomson, aye.

MR. LANGFORD: Langford votes no.

MR. BUCKHEIT: Buckheit, aye.

MR. LANGFORD: Mr. Hanson?

MR. HANSON: No.

MR. LANGFORD: Okay. So the HCl limit in the permit Condition 13 of the MACT permit for

hydrogen chloride three-hour average is hereby reduced from the .0066 to .0029 pounds per million BTU.

MR. BUCKHEIT: If I could just amplify a point -- I am not rearguing the motion -- it is just the litigants who would seek to upset the permit -- they may want to argue that we have to look at all units.

MR. LANGFORD: Uh-huh. I'm just trying to --

MR. BUCKHEIT: But bear with me -- if they win, it doesn't matter on the mercury side, because I believe the CFB units are the best performing of all of the units.

But then we would be overturned on the HCl side, and have to go back at it, even when it didn't matter, you know.

MR. LANGFORD: And the hypothetical case is exactly the opposite -- the permittee could challenge us that we went beyond the floor without any rationale, and it could be overturned on that basis.

So, I mean, we have got a risk either way.

MR. BUCKHEIT: Fair point.

MR. LANGFORD: Any final amendments to make?

MR. MOORE: I would move that we remove the 72 pounds in the PSD permit. I want to leave the cross linkage.

I don't know whether that means you leave the line there or not, but I feel very strongly that we should not have that 72 pounds there. I think it is --

MR. LANGFORD: We are referring to the emissions limits in the PSD permit, and I'm looking for the right one and I haven't found it yet.

MR. MOORE: It is page nine, limit 29.

MR. LANGFORD: All right. Here it is.

All right. I would like the staff's help on this. I would like to leave the linkage.

So you tell us what we need to do there so there will be a reference there.

MR. LANGFORD: I believe -- let me try to help you, Mr. Feagins -- the note under each boiler, F and G -- F -- the F note relates to how to calculate the weight of emission limit for each CFB, using a formula. And I don't think we're talking about doing anything with

that -- leaving that.

Note G is the one that says: Shall comply with the MACT permit.

So I think what we are talking about doing -- if this meets your need Mr. Moore -- is removing -- it has already got the "G" -- Note G, but removing the 7193, and just replacing that with Note G.

MR. MOORE: Is "F" used anywhere else, Mr. Feagins?

MR. FEAGINS: I don't believe it is, Mr. Moore.

MR. MOORE: We don't need "F" do we?

MR. FEAGINS: If you take the limit out, you do not need "F."

MR. MOORE: Well, that is what I thought.

MR. FEAGINS: So why don't we just say in a Note G for both the each boiler and combined total emission limit?

MR. MOORE: I think, really all you need to do is why don't you put the word "note" under "each boiler" and on the "combined total" and change Note G and make it "F" because before we have eliminated "F."

So "G" would come out, and there would

just be a note at each place there, and "G" cross references the new permit; correct?

MR. FEAGINS: Mr. Langford, could I ask a question?

MR. LANGFORD: Yes, sir.

MR. FEAGINS: If the limit is removed, would it not be appropriate to remove the word "mercury" as well since there is no limit and use some other mechanism used to construct that footnote?

MR. BUCKHEIT: Why wouldn't we just have a general provision -- because it is not just mercury you're talking about -- it is HCl HF and CL -- a general provision that says the MACT permit shall be complied with?

MR. FEAGINS: Because there is a --

MR. BUCKHEIT: Under our state authority.

But you're not saying it is BACT. I'm not saying that.

MR. FEAGINS: Well, HCl and HF.

MR. BUCKHEIT: No, but I'm not suggesting any statement that in the BACT section you say anything.

MR. FEAGINS: Right.

MR. BUCKHEIT: But this would be like a

state operating permit, where you would simply say, someplace outside of the BACT thing -- and I am not even looking at the structure -- of course you will comply with the MACT.

MR. FEAGINS: Well, the MACT and the PSD permit?

MR. BUCKHEIT: In the PSD permit, you say, "and of course you comply with the MACT permit."

In issuing the PSD permit, don't you have to certify that it complies with the MACT?

Isn't there a stand-alone requirement to certify that the PSD construction permit -- not the PSD construction permit, but that the permittee will comply with MACT and that is why you --

MR. FEAGINS: There is a statement in the introduction to the permit or in the cover letter or in both that says: The permittee is expected to comply with all applicable requirements and permits.

MR. BUCKHEIT: I thought under the MACT rules that you were required -- in most cases -- in a case-by case, the MACT is not actually in the permit. It is a declaration drafted by

you that the permittee will comply with MACT.

MR. FEAGINS: Well, they would have been incorporated by reference and specifically.

MR. BUCKHEIT: So is there some reason we just couldn't say, "In the construction permit"?

MR. FEAGINS: Well, what I would propose as an alternative, if Mr. Moore, and Mr. Langford would agree, is that we leave a generic footnote in, and that would be Footnote G as we have it there, and remove Footnote F, and remove the limit, and remove the word "mercury."

And that way, the footnote survives in Condition 29.

MR. MOORE: Well, what worries me about that is, someone says: Oh, you took the limit out.

And the answer is: No, because I think Footnote G probably meets the change because it envisions a limit here.

It probably should say: The permit shall comply with the mercury emission rate limit set in the MACT permit issued -- they both can be issued the same day; correct?

MR. FEAGINS: They could be.
So you would be comfortable putting Footnote G as an appendage to the word "mercury"?
MR. MOORE: Yes. Because it refers to mercury.
And if somebody says, "Well, you took the limit out," we will say, "No, we took care of that in this other permit to make sure there wasn't any misunderstanding."
MR. FEAGINS: I am completely comfortable with that, Mr. Moore.
MR. LANGFORD: Well, let me throw a wrench in the works.
Because now we -- in the MACT permit, we have now changed the hydrogen chloride number and the carbon monoxide number, and now we have different numbers here than we do over there.
Right?
MR. FEAGINS: Yes. You have different determinations based on the BACT and MACT.
MR. LANGFORD: The same thing we did with mercury. I mean, we have a different determination for mercury then we did -- over in the MACT permit than we did here.

Now we have got a different -- now we changed the MACT number for C0. It still shows the .15 here. And hydrogen chloride still shows the double oh 66.

We just changed both those numbers in the MACT permit.

Do we need to do something here -- put a note in or something?

MR. FEAGINS: No, not necessarily, is the short answer.

If you establish those numbers, as you have in the MACT permit, then those numbers would prevail -- the most stringent numbers prevail. And they have to comply with both permits.

MR. LANGFORD: Which was the same argument on mercury, but nobody liked it.

MR. GREGORY: The difference with mercury is that mercury was struck from -- where we originally had mercury based on the 111 requirement, and that it is a subpart D-8 pollutant.

That argument that it was removed from 111, and therefore isn't in the realm of PSD is really the argument Mr. Moore is making and the

point that Cale Jaffe and others have argued.
But HF and HCl are specifically --
MR. LANGFORD: We didn't change the HF. We change the HCl. The HCl number here is no longer the applicable limit.
MR. FEAGINS: We are just calling attention to the two pollutants as examples of being PSD pollutants. They remain PSD pollutants.
MR. LANGFORD: Do you need essentially the language in Note G, which says either this permit or the other one -- most stringent, to be a superscript on those two numbers?
MR. FEAGINS: I don't believe it would detract from the PSD permit to have that footnote.
MR. LANGFORD: In the same way that we are talking about you have to look somewhere else to get the real number?
MR. FEAGINS: That's correct.
MR. MOORE: Mr. Langford, I will accept that as a friendly amendment and what this means that we will have notes -- both notes involving the ones that are in both places, they will be one note -- a note.

And for mercury, there will be the Note G, rewritten to say it is not the most stringent of the two, it is the MACT limit, and the limit will come out, but mercury will be listed.

MR. FEAGINS: The most direct way to do this and to take care of Mr. Langford's concerns, and yours, Mr. Moore, would be to go to Footnote G and remove the word "mercury."

And it would say then, "the permittee shall comply with the most stringent emission limitation as may be contained in this permit or any similar permit in effect and applicable to the source," and then append "carbon monoxide, hydrogen chloride and mercury" with that Footnote G.

MR. MOORE: And that is the way you referred to a MACT permit in article seven.

MR. FEAGINS: That's the way we chose to do that.

MR. MOORE: Okay. I'm not -- I just want to make sure that I understand.

That's the way you say "in the MACT permit."

MR. FEAGINS: Yes. Article 7.

MR. LANGFORD: I am okay with that.
MR. MOORE: I move what he said.
MR. BUCKHEIT: I second it.
MR. LANGFORD: Any other discussion?
Hearing none, I'll ask for a voice vote on this one. All in favor say aye.
MR. BUCKHEIT: I think we need a little clearer on the motion -- what it is now that Mr. Moore agrees with -- so the transcript --
MR. MOORE: Well, really what Mr. Feagins said.
We will delete the 72 pound number.
MR. LANGFORD: For the record, 71.93.
MR. MOORE: 71.93. And we will have a footnote -- we will delete what is now Footnote F, and Footnote G, which may be relettered, if that's appropriate, will be revised so as to state that it is the most stringent of either the PSD or MACT permit that controls.
And obviously, for mercury, that will be the MACT because there is no limit here, and for the others, there are two limits.
Did I say that correctly, Mr. Feagins?
MR. FEAGINS: I believe that's equivalent to Footnote G.

MR. MOORE: All right. Thank you.
That's what I move.
MR. LANGFORD: Having been interrupted, we will try again on the call for the vote.
All in favor say aye.
MR. MOORE: Aye.
MS. THOMSON: Aye.
MR. BUCKHEIT: Aye.
MR. LANGFORD: Aye.
MR. HANSON: Aye.
MR. LANGFORD: Opposed say no.
Hearing none, the motion is carried.
Any other amendments to the main motion?
Hearing none, any discussion on the main motion -- that main motion being to issue the two permits, PSD and MACT permits for the Dominion Virginia City Hybrid Energy Center as amended by the various amendment that we have taken up this afternoon.
Discussion on that?
MS. THOMSON: I would just like to make a couple of final comments.
MR. LANGFORD: Yes, Ms. Thomson. Go ahead.
MS. THOMSON: We have heard a lot of

concerns expressed on many sides as we have undertaken this process. There are just a couple of concerns I would like to address -- and I hope describe what, at least is in my mind, with respect to these.

In the comments, it was pointed out that Southwest Virginia suffers disproportionately from certain ailments.

There are many studies, apparently documenting these effects, and one of the most recent was a Harvard study that showed that among other areas in the country, several counties in Southwest Virginia are among those in which life expectancy declines for women, were observed between 1983 and 1999.

The kind of illnesses that appear to be associated with these so-called reversal of fortune counties here and elsewhere are among those that are exacerbated by air pollution.

For example, many studies have shown a link between premature mortality, respiratory disease and cardiovascular problems on the one hand and exposure to the kind of air pollutants we have regulated here today on the other hand.

I believe that the standards we have set

for today will minimize the additional risks imposed on the people here in Southwest Virginia from the pollutants we have regulated under the Clean Air Act.

I would just like to talk briefly about the term "environmental justice," which has also been raised.

Again, this was raised because the southwest portion of Virginia has lower per capita incomes and shows a higher percent of the population in poverty relative to the rest of the Commonwealth.

According to US EPA, environmental justice is the fair treatment and meaningful involvement of all people, regardless of race, color, national origin, or income with respect to the development, implementation, and enforcement of environmental laws, regulation and policies.

Now EPA has not codified a set of principles in rule making, but I would submit that in providing the ample opportunity for public participation that we have done in this action in Southwest Virginia and elsewhere in the Commonwealth, I believe we at least

followed the spirit of EPA in conjunction with environmental justice guidance on participation.

I would just like to end with -- I believe that obviously this follows my comments earlier that we have established strong appropriate standards that follow the letter of the federal and Virginia law. And I would add I think that we have done so expeditiously in keeping with the desires -- the expressed desires of members of the General Assembly and Governor Kaine.

MR. LANGFORD: Are there other discussions of the motion?

John, did you have anything you wanted to say?

MR. HANSON: I do not.

MR. LANGFORD: Seeing no on else, let me make a couple of comments.

We have heard several times that this plant will have the best suite of controls ever built, I guess, probably in -- certainly in the U.S, and maybe anywhere.

The need for continued energy is a great one. We have great energy needs both in the

electricity sector as well as the public transportation sector with gasoline and others. And I think given the vast coal reserves that the United States and particularly in Virginia have, that it is a good decision to utilize those coal reserves to generate electricity.

This suite of controls and now this set of emissions standards, emission limits, that we have provided, I think will also be some of the most stringent in the country, and will set a standard for the future power plant construction that may go forward.

And so in that regard I am very pleased to be a part of that.

I know that some of our commenters have been concerned about carbon dioxide, the effects of a coal-fired plant versus alternative fuels, and the effect that this particular plant with its now extremely small carbon -- sorry, not carbon -- but sulfur dioxide emissions will have, I think -- I just don't agree with that, given the fact that there are reports that in the -- in China, for example, they are actually starting up a new coal-fired power plant every two weeks.

And this is going to be one of the first ones built in the U.S. in a long time.

And I do not know the limits that they're using in China, but I am guessing that they are not as stringent as those that are done here.

And so for that reason, I feel very comfortable in voting to approve this permit. I think we have got the best permit that is going to be protective of human health and the environment, and one that does meet the laws and regulations that are required to be done.

So having said that, is there anybody else that has any comments?

MR. BUCKHEIT: I guess I'll offer a soliloquy.

MR. LANGFORD: Hmm?

MR. BUCKHEIT: I guess I'll offer a soliloquy, but I'll keep it short, because everybody is tired.

I'm as strongly committed to a carbon tax and climate change legislation as anyone.

But the political consensus isn't there yet in the country. We have to work to build that consensus. I think that voting against this particular permit on carbon issues would

have been counterproductive to the overall effort to get federal legislation. I think it would have caused a backlash. I think a backlash also would be caused if we started experiencing brownouts. We need power in this country, and if we start having brownouts, we will quickly lose any political support that we might need to get effective carbon legislation.

You saw us be mindful here, take opportunities as they presented themselves to, you know, get at biomass, get at efficiency. We certainly considered it. We didn't establish a BACT limit for it, but I think that Virginia policy as set out by the legislature and the governor specifically supported this particular plant, so it is a different situation then you had in Kansas and elsewhere. And we all need to work to get a consensus together to make the changes to get real steps taken, to get the steps to get at the climate change issue.

MR. MOORE: Mr. Chairman, just very briefly, I think we have done today, what the law requires. We have looked at these issues. We have weighed them. We have obeyed the

Clean Air Act and the Virginia statutes.

And I think the Commonwealth will be better for it.

I particularly appreciate my colleagues -- all of them. I think we have worked well together today, discussing the issues coming to consensus on many many issues.

And I think that that speaks well for the system -- the fact that we have had very strong debate, that we had disagreement on a number of issues, but this board was able to basically come together on most of them.

And I thank my colleagues for that.

MR. BUCKHEIT: I would also offer thanks to the staff for putting up with us.

We argue, we debate, we battle and we come to a resolution, but we respect each other, and I certainly respect the work that the staff puts in for us, for they are as committed as we are to protecting Virginia's environment.

Sometimes we have different thoughts about it -- how far the role of the agency extends, but that is not a personal issue.

MR. LANGFORD: John, do you have anything

you want to say before we call a vote?
MR. HANSON: No. I think it has all been said. I would like to vote.
MR. LANGFORD: I think there is a lot of people that would like us to vote.
All right. The motion is to -- that is on the table is to approve the Dominion Virginia City Hybrid Energy Center PSD and MACT permits as amended today, and various amendments that were previously done.
And I'll ask for votes from my left.
Mr. Moore?
MR. MOORE: Moore, aye.
MS. THOMSON: Thomson, aye.
MR. BUCKHEIT: Buckheit, aye.
MR. LANGFORD: And Langford votes aye.
MR. HANSON: Aye.
MR. LANGFORD: And the motion is carried, and by that means we direct the staff to go ahead and make those changes, and move forward with those permits.
And having no further business, I don't think in front of us -- unless -- Mr. Josephson is looking at me.
MR. BUCKHEIT: Just a procedural. Just

to understand what is going to happen here.

The staff will go off and wordsmith up a permit. And I think what the discussions have been is that they will send the proposed language to the members to initial off on, as soon as they are able. And thereafter, Mr. Paylor will issue the permit.

MR. LANGFORD: That may have been your discussion. I am perfectly satisfied with the information that we have given and I am comfortable that the staff will do it, and I, for one, would prefer to see staff just go ahead and make -- in their routine course of business, make their changes and move forward with it.

I don't think we need to delay a day or two or however long it is going to take to try to get individual board members to start weighing in and wordsmithing on the permit.

I think we have gotten all the main points covered, and I trust staff to get it taken care of.

MR. BUCKHEIT: We have had it happen before where there was a communication failure.

MR. LANGFORD: I stand by my comments.

MR. BUCKHEIT: I move that that -- the procedure that I set out be the procedure going forward.

MR. LANGFORD: Is there a second?

MR. MOORE: I have got to second that. I do not want to slow the process down. I think -- what I hope the staff will do -- if they will do this, they can send it to us, particularly, if you have any question about something -- you know, hey, now that we think about it, there are two ways to do that, you know, talk to Mr. Paylor about that and he can talk to some folks on board and we can, you know, we'll be able to work it out.

MR. LANGFORD: We do have a motion and a second.

Mr. Paylor would you like to explain?

MR. PAYLOR: My primary concern with that is I believe we have captured the essence here, and I don't anticipate any trouble, but if we have multiple board members wordsmithing in different directions, the staff will be unable to move forward.

One option might be for us to have the Chair as the one with whom we discuss any

miscommunication that might have been part of our --

MR. BUCKHEIT: I'm not talking about a wordsmithing exercise.

I am talking about a -- I assume -- I don't have any time or energy to participate in the drafting exercise.

MR. PAYLOR: I am simply anticipating, Mr. Chair, that if we get conflicting comments from board members, we will be stuck and not be able to move the permit forward.

MR. LANGFORD: Thank you, Mr. Paylor.

My comment to the motion and the second is I know what Mr. Moore says -- he doesn't want to delay the issuance of the permit, but this motion will delay the issuance of the permit, if not by a day or two -- a week -- I'm not sure how long, but it is going to add another step, and therefore add more time. And I for one am fully confident that the staff can do it properly and they have taken good notes and we have the transcript if Ms. Berndt needs to do it, and there have been consultation on the breaks to clarify any points.

I have no qualms at all about that.

MS. THOMSON: I share that. I share that confidence.

MR. MOORE: Mr. Chairman, I seconded the motion. I shall vote against it. Hearing Mr. Paylor, if he thinks he has got it all straight, and he doesn't have a problem with it, I'll take that.

MR. LANGFORD: All right. Let's have a vote on a motion to have a --

MR. BUCKHEIT: I'll withdraw the motion.

MR. LANGFORD: Okay. The motion has been withdrawn.

Okay. Any other points that need to be resolved?

Hearing none, this meeting of the State Air Pollution Control Board is adjourned.

(Whereupon, the proceedings concluded at 5:15 p.m.)

COMMONWEALTH OF VIRGINIA AT LARGE, to wit:

I, Caroline Lane, Court Reporter, Notary Public in and for the Commonwealth of Virginia at Large, and whose commission expires February 28, 2011, do certify that the foregoing is a true, correct, and full transcript of the proceedings adduced.

I further certify that I am neither related to nor associated with any counsel or party to this proceeding, nor otherwise interested in the event thereof.

Given under my hand at Roanoke, Virginia, this 8th day of July, 2008.

_____

Caroline Lane, Notary Public
Notary Registration No. 238126
Commonwealth of Virginia at Large

G

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Dominion Virginia City Hybrid Energy Center
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Dear Air Pollution Control Board of the Virginia Department of Environmental Quality:

I am an environmental engineer with over 30 years of experience in Clean Air Act permitting, including BACT and MACT analyses for over 75,000 MW of coal, gas, wood, oil and other power plants. I submit these comments on my own behalf. I address two MACT issues raised by Mr. Buckheit in his April 14, 2008 memorandum to Board Members ("Buckheit Memo").

MACT

PM As A Surrogate For Metal HAPs

Mr. Buckheit notes that VDEP's MACT analysis assumed high control efficiencies for metal HAPs based on the use of particulate matter as a surrogate, but provided nothing to support the assumed 99.7% to 99.9% control efficiencies into a PM MACT limit. Buckheit Memo at 15. I agree. These assumptions are not likely to be met in practice unless the baghouse is designed to meet them and they are required as permit limits, or are converted into HAP-specific permit emission limits.

First, most metallic HAPs are volatilized in the boiler and condense as very fine particulate matter or nanoparticles (<2.5 microns) in the pollution control train. Ex. 1.[1] The highest concentrations are consistently found in the

[1] R.C. Flagan and S.K. Friedlander, Particle Formation in Pulverized Coal Combustion – A Review, In: *Recent Developments in Aerosol Science*. D.T. Shaw (Ed.). 1978, Chapter 2 (Ex. 1A); A.S. Damale, D.S. Ensor, and M.B. Ranade, Coal Combustion Aerosol Formation Mechanisms: A Revieiw, Aerosol Science & Technology, v. 1, no. 1, 1982, pp. 119-133. See also: S.K. Friedlander, *Smoke, Dust, and Haze. Fundamentals of Aerosol Dynamics*, 2nd Ed., Oxford University Press, 2000.

smallest particles. Exs. 2,[2] 3.[3] The particulate collection efficiency for conventional baghouses designed to collect PM and PM10 is generally lower for these nanoparticles that contain most of the metallic HAPs than for larger particles.[4] Ex. 3, p. 1538; Ex. 4,[5] p. 1582. Thus, a fabric filter system designed to meet BACT for PM and PM10, as is the case here, does not necessarily meet MACT for metallic HAPS as these are present in particles smaller than 10 microns which are not as effectively controlled. These smaller particles also cause proportionately more of the adverse health impacts because they can penetrate deep into the lung. Ex. 4.

Second, not all HAPs condense and are present as fine particles that can be captured by a baghouse. Selenium is the most problematic as 50% to 100% of the selenium in coal is present as a vapor in exhaust gases. Further, depending upon the fuel and control train, some of the otherwise nonvolatile trace metals, including chromium and nickel, may be present in the vapor phase. Finally, mercury controls, including powdered activated carbon and sorbent enhancements, have been demonstrated to increase the amount of chromium and nickel in stack gases, compared to no mercury control.[6]

Thus, it is premature to conclude that particulate matter is a reasonable surrogate for HAPs, especially based only on conventional baghouse control. Other technology may be required to control volatile metallic HAPs. Further, much higher control efficiencies can be achieved for particulate HAPs using advanced filtration media and wet electrostatic precipitators, among others. Permit limits should be established for each individual HAP to assure that MACT is required.

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[2] Richard L. Davidson and others, Trace Elements in Fly Ash, *Environmental Science & Technology*, v. 8, no. 13, December 1974, pp. 1107-1113 (Ex. 2A); E.S. Gladney and others, Composition and Size Distribution of In-State Particulate Material at a Coal-Fired Power Plant, *Atmospheric Environment*, v. 10, 1976, pp. 1071-1077 (Ex. 2B): John M. Ondov, Richard C. Ragaini, and Arthur H. Biermann, Emissions and Particle-size Distributions of Minor and Trace Elements at Two Western Coal-fired Power Plants Equipped with Cold-side Electrostatic Precipitators, *Environmental Science & Technology*, v. 13, 1979, pp. 946-953 (Ex. 2C).

[3] W.P. Linak and others, Comparison of Particle Size Distributions and Elemental Partitioning from Combustion of Pulverized Coal and Residual Fuel Oil, *J. Air & Waste Manage. Assoc.*, v. 50, 2000, pp. 1532-1544.

[4] AP-42, Table 1.1-5,

[5] JoAnn S. Lighty, John M. Veranth, and Adel F. Sarofim, Combustion Aerosols: Factors Governing their Size and Composition and Implications to Human Health, *J. Air & Waste Manage. Assoc*, v. 50, 2000, pp. 1565-1618.

[6] McIlvaine Hot Topic Hour, Hazardous Air Pollutants, May 15, 2008, Presentation of John Pavlish, EERC. Voice recording available online to subscribers of McIlvaine Power Plant Knowledge System and available for purchase.

Baghouse Design

Mr. Buckheit states that the best baghouses have an air to cloth ("A/C") ratio of less than 2:1 (presumably 2 ft/min). Buckheit Memo at 16. However, fabric filter design to achieve the high filtration efficiencies assumed for HAPs is a bit more complex, requiring specification of grain loading, control efficiency, type of bag cleaning, filtration media, etc. The stated A/C of less than 2 ft/min is typical for reverse air fabric filters. However, pulse jet fabric filters, proposed here, typically operate at 3.0 to 4.0 ft/min. Steam[7] at 33-10.

Fabric filter baghouses are only as efficient as the bags they use. The filtration media determines the control efficiency of a baghouse for very small particles. There is a wide range of media that can be used, most of which are more efficient for larger particles. The design basis filtration media (Ryton is a type of material, not the design basis media) for the proposed baghouse is unknown and should be determined. The exhaust gas conditions should allow wide latitude in selection of filtration media to achieve high removal of the smallest particles where metallic HAPs are concentrated.

Media have been developed over the last decade that remove over 99.99%+ of the 2.5 micron particles. These include Daikin's AMIREX™, PTFE membrane filters[8] and W.L. Gore's L3650.[9] See summary of U.S. EPA's ETV test results in Exhibit 5. The BACT and MACT analyses do not identify the type of filtration media that are assumed nor the removal efficiency as a function of particle size, which are required to determine if MACT for metallic HAPs has been required.

Phyllis Fox

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[7] Babcock & Wilcox CO., *Steam. It's Generation and Use*, 41st Ed., 2005.

[8] McIlvaine Hot Topic Hour, Filter Media Selection for Coal-Fired Boilers. September 13. 2007, Presentation by Todd Brown. Daikin America, Inc. Voice recording available online to subscribers of McIlvaine Power Plant Knowledge System and available for purchase.

[9] USEPA, ETV Joint Verification Statement, Baghouse Filtration Products, W.L. Gore & Associates, L3650 .at http://epa.gov/etv/pubs/600etv06042s.pdf.

EX 1A

RECENT DEVELOPMENTS IN AEROSOL SCIENCE

Edited by

DAVID T. SHAW

State University of New York at Buffalo

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2. D. Grosjean and S. K. Friedlander, *JAPCA*, **25**, 1038 (1975).
3. R. C. Flagan and S. K. Friedlander, "Particle Formation in Pulverized Coal Combustion—A Review," Chap. 2 this volume.
4. S. K. Friedlander, *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior*, Wiley-Interscience, New York, 1977.
5. C. T. R. Wilson, "On the Cloud Method of Making Visible Ions and the Tracks on Ionizing Particles," in *Nobel Lectures in Physics 1922–1941*, 1927.
6. J. Frenkel, *Kinetic Theory of Liquids*, Dover, 1955.
7. B. J. Mason, *The Physics of Clouds*, Clarendon, Oxford, 1971.
8. P. P. Wegener and A. A. Pouring, *Phys. Fluids*, **7**, 352 (1964).
9. R. H. Heist and H. Reiss, *J. Chem. Phys.*, **59**, 665 (1971).
10. P. T. Roberts and S. K. Friedlander, *Environ. Health Perspect.*, **10**, 103 (1975).
11. S. P. Sander and J. H. Seinfeld, *Environ. Sci. Technol.*, **10**, 1114 (1976).
12. J. G. Calvert, "Interactions of Air Pollutants," in *Proceedings of the Conference on Health Effects of Air Pollutants*, U.S. Government Printing Office No. 93-15, 1973.
13. H. Reiss, *J. Chem. Phys.*, **18**, 840 (1950).
14. D. Grosjean, personal communication, 1975.
15. C. S. Kiang and D. Stauffer, *Faraday Symp. Chem. Soc.*, No. 7, 29 (1973).
16. P. Mirabel and J. L. Katz, *J. Chem. Phys.*, **60**, 1138 (1974).
17. N. A. Fuchs and A. G. Sutugin, "High-Dispersed Aerosols," in G. M. Hidy and J. R. Brocks, Eds., *Topics in Current Aerosol Research*, Pergamon, New York, 1971.
18. P. H. McMurry, "On the Relationship between Aerosol Dynamics and the Rate of Gas-to-Particle Conversion," Ph.D Thesis in Environmental Engineering Science, California Institute of Technology, Pasadena, Calif., May 2, 1975.
19. W. D. Scott and P. V. Hobbs, *J. Atmos. Sci.*, **24**, 54 (1967).
20. C. E. Junge and T. G. Ryan, *Q. J. R. Meteorolol. Soc.*, **84**, 46 (1958).
21. J. Freiberg, *Environ. Sci. Technol.*, **8**, 731 (1974).
22. K. G. Denbigh, *The Principles of Chemical Equilibrium*, 2nd ed., Cambridge University Press, New York, 1966.
23. J. R. Brock, *Atmos. Environ.*, New York, **5**, 833 (1971).
24. J. L. Katz, C. J. Scoppa, N. G. Kumar, and P. Mirabel, *J. Chem. Phys.*, **62**, 448 (1975).
25. S. L. Heisler and S. K. Friedlander, *Atmos. Environ.* **11**, 185 (1977).

CHAPTER 2 PARTICLE FORMATION IN PULVERIZED COAL COMBUSTION—A REVIEW

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1. NOMENCLATURE

C_i	concentration, molecules cm^{-3}
$\bar{C}$	concentration in fly ash
C_0, C_s	coefficients
d, d_p	particle diameter
D	diffusivity
F	diffusion flux to particle surface
I_1, I_2, I_3	moments of free molecule regime self-preserving size distribution
I_D	integral for diffusion to surfaces of large particles
K	coefficient, defined by Eq. 12
Kn	Knudsen number
k	Boltzmann constant
M	total mass per unit volume
m	mass of gas molecule
$\tilde{N}(t)$	total number of particles per unit mass at time t
$n(v,t)$	particle size distribution function, particles $cm^{-3}cm^{-3}$
$n(d_p)$	particle size distribution function, particles $cm^{-3}cm^{-3}$
$\tilde{n}(v,t)$	particle size distribution function, particles $cm^{-3}cm^{-3}$
P	pressure
p	number of ash particles produced per coal particle
R	gas constant
T	temperature
t	time
u	gas velocity
$\tilde{V}$	total aerosol volume, cm^3g^{-1}
v	particle volume
α	mass fraction ash in coal
α_c	accommodation coefficient
α_v	volume fraction ash in coal
$\beta(v,v')$	collision parameter
η	dimensionless particle volume
λ	mean free path
τ	time parameter, defined by Eq. 12
$\Psi(\eta)$	dimensionless distribution function

Subscripts

a	ash
c	coal
l	large particles produced by breakup
r	particle
s	small particles produced by homogeneous nucleation

2. INTRODUCTION

Particulate emissions from coal combustion sources were among the first forms of air pollution to be controlled. The opacity of stack plumes and the total mass of particulate matter emitted have been significantly reduced through improvements in combustor operation and the use of gas cleaning devices such as electrical precipitators. In spite of these improvements, coal combustion is still a major source of particulate emissions. Moreover, electrical precipitators may show a minimum in collection efficiency for particles in the 0.1–1.0 μm size range [1]. Such particles have longer atmospheric residence times and greater effects on health and visibility than would an equal mass of larger particles.

Coal combustion is an important source of heavy metals in the environment [2–9]. Many species, including cadmium, arsenic, selenium, lead, nitrogen, zinc, and antimony, are present in the fly ash particles emitted by coal fired power plants and in ambient urban aerosols in concentrations much larger than their natural crustal abundance [10] as shown in Fig. 1. Recent studies have shown that the concentrations of several trace species in fly ash increase with decreasing particle size [11–17]. Few measurements of ash size distributions have been made using techniques suitable for particles smaller than about 5 μm diameter [18]. Studies of the fractional efficiency of particle collection equipment have recently provided some more complete size distribution data [1, 19, 20]. Data on the composition-size distribution have been obtained for few sources and have not been extended far into the submicron size range.

The composition-size distributions of particles emitted by coal combustion sources are influenced by furnace design and operating conditions. A wide variety of coal combustion equipment is currently in use. New designs are being developed because of recent constraints on emissions of gaseous and particulate pollutants and on fuel availability. Electrostatic precipitator performance may be seriously impaired when a low sulfur coal is substituted for a coal with a higher sulfur content and correspondingly lower resistivity ash. Fabric filters may replace electrical precipitators for particle collection where low sulfur coal is burned. Some combustion modifications may change the quantities of fine particles in the flue gases. To anticipate the future requirements for particulate emission control and

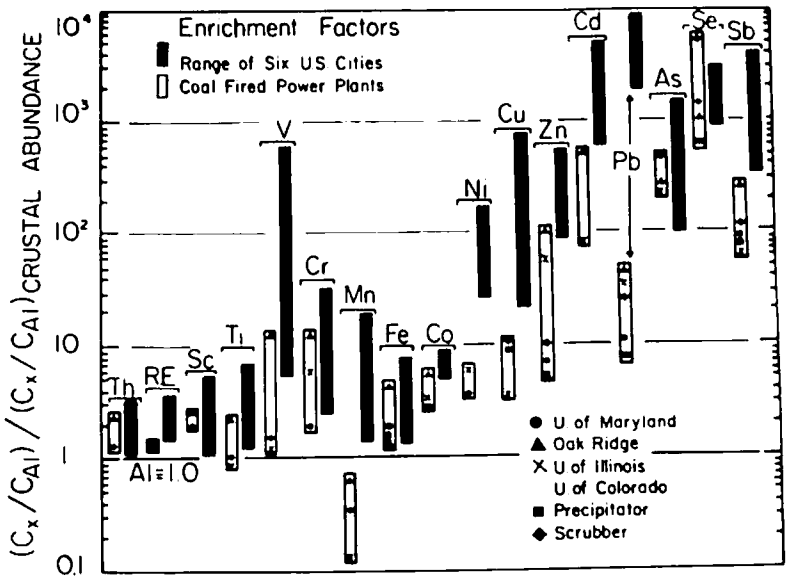

Fig. 1. Enrichment factors for several elements on ambient particles collected in several U.S. cities and on particles collected downstream of gas cleaning devices on coal fired power plants. Enrichment is calculated relative to the natural crustal abundance of the elements. (Data from Ref. 10.)

to evaluate the environmental impact of increased coal use, it is necessary to know the characteristics of the aerosol entering the gas cleaning devices. An examination of the mechanism of particle formation during coal combustion may provide much of the necessary information.

Emissions from coal combustion may include several types of materials, such as char, soot, fly ash, and droplets containing sulfuric acid. Improvements in combustion conditions have, in recent years, reduced the amount of partially burned coal char emitted from utility boilers. The combustible content of the particulate emissions from large sources generally accounts for only a small fraction of the total mass of emissions [11, 21]. Soot is formed by the condensation and subsequent pyrolysis of high molecular weight hydrocarbons [22, 23]. Fly ash is formed from the mineral matter in the coal. During combustion the mineral matter undergoes chemical transformations to form ash and, if temperatures are sufficiently high, the ash fuses to form spherical particles [24–34]. Some ash may be vaporized in the high temperature flame region and later condense homogeneously to

form large numbers of very small fly ash particles [35–37]. Submicron fly ash particles may also be produced by the bursting of bubbles as gases are evolved within molten ash particles [28, 29].

The presence of sulfur trioxide (SO_3) in the flue gases of coal fired boilers results in the formation of alkali metal sulfates or sulfuric acid when it condenses [37]. The homogeneous oxidation of sulfur to form SO_2 is fairly well understood [38]. Less is known about the mechanism of SO_3 formation. Generally about 1% of the sulfur is present in the flue gases as SO_3 [38]. As the flue gases cool, this SO_3 may condense with water vapor to form sulfuric acid droplets. Stack temperatures are usually maintained above the dew point of the SO_3–H_2O mixture to prevent acid condensation within the stack.

Studies of the occurrence of deposits in boilers [37] and microscopic examinations of fly ash particles [24–34] provide the basis for a preliminary analysis of fly ash formation and identify some of the important processes that occur. The present study is restricted to the examination of particle formation in pulverized coal fired systems. This is the predominant method of coal combustion for electric power generation. Moreover, most of the available data on particle formation and emissions have been obtained on pulverized fuel equipment.

3. PULVERIZED COAL COMBUSTION

Pulverized coal fired boilers burn coal that has been crushed and ground to a fine powder [39, 40]. The mass mean diameter of the coal particles is typically in the range of 30 to 70 μm. The distribution of coal sizes is broad. A coal powder with a 50 μm mass mean diameter may have 10% of the mass smaller than 10 μm and 10% larger than 100 μm. The few reported measurements of coal size distributions indicate that the distribution varies significantly from one power plant to another [41]. Coal burned in a suspension at 1800–2500°K must remain at high temperature long enough for the largest particles to burn completely. About 1 sec is required to burn a 200 μm diameter coal particle. Smaller particles burn much more rapidly.

Pulverized coal fired boilers are generally large; units producing 500 MW electrical output are common. Many furnaces larger than about 600 MW are divided into two combustor chambers. Pulverized coal is injected into the furnace with about one-fifth of the total air flow, the primary air, through a number of burners [39]. A 500 MW boiler, illustrated in Fig. 2, may have 30 or more burners arranged in one of a number of possible patterns in the furnace walls. Preheated air is introduced into the furnace through air registers coaxial with the burners. In the furnace the coal is heated by thermal radiation and by mixing with hot combustion products,

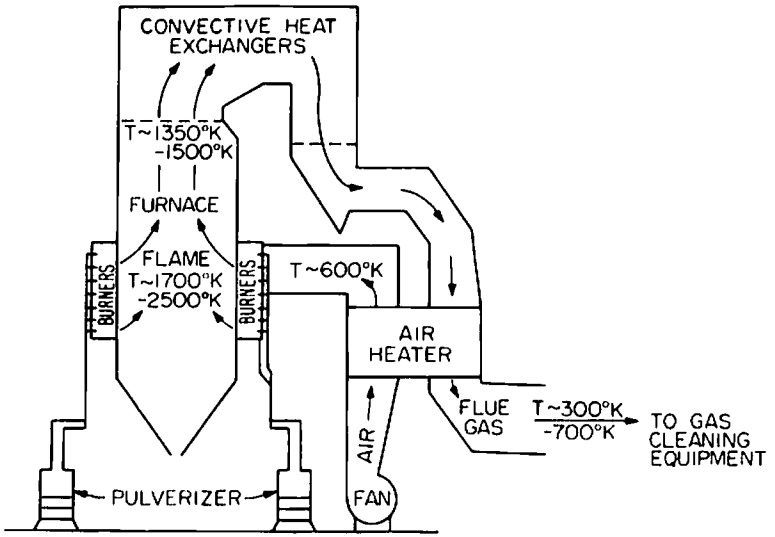

Fig. 2. Pulverized coal fired boiler.

igniting the coal particles. The temperatures of the burning coal particles and the gas surrounding them rise rapidly. Mixing in the furnace is relatively slow. As a result, the temperature and composition of the combustion gases are far from uniform. Although peak temperatures may be as high as 2500°K, some coal particles may be subjected to much lower combustion temperatures. The variability in time–temperature history of the coal particles may be responsible for much of the diversity of ash characteristics observed in the emissions from a combustion system. A complete representation of the kinetic processes occurring in a furnace would require a statistical description of the composition and temperature fluctuations and the residence time distribution in the boiler [42, 43].

In the furnace the temperature of the combustion products is reduced by the combined effects of radiation and convective heat transfer. About one-half of the heat released during combustion is transferred to the water tube walls of the furnace before the combustion products enter the convective heat exchangers. The temperature at the furnace outlet is limited to about 1350–1500°K in order to prevent damage to the superheater tubes. A long residence time of the combustion gases in the boiler, about 1 to 2 sec, is necessary to assure both complete combustion and adequate heat transfer upstream of the superheaters.

A typical 500 MW pulverized coal fired electric power plant has a furnace about 30 m high with a cross-sectional area of about 260 m^2 [44].

Operating at about 35% thermal efficiency, this unit requires about 1430 MW of thermal input, for instance, approximately 48 Kg sec^{-1} (170 T hr^{-1}) of a bituminous coal with a lower heating value of 3×10^{7}J kg^{-1} (12900 Btu lb^{-1}). Burning a coal containing 10% ash, this unit produces about 4.8 kg sec^{-1} (17 T hr^{-1}) of ash. If all the ash were carried out of the furnace in the flue gases, the aerosol mass loading would be about 9 g m^{-3} at standard conditions.

Pulverized coal is burned in a variety of types of combustors. The peak temperatures and the amount of ash impacting on the boiler walls are strongly influenced by the furnace design. Some units, designed to achieve rapid mixing of fuel and air, result in high combustion intensities and thus high flame temperatures. Boilers in which fuel and air mix relatively slowly have lower flame temperatures. Because nitric oxide emissions increase at high temperature, the latter designs are being favored for new installations. Cyclone burners were designed to remove most of the ash from the flue gases before they enter the superheaters where deposits cause reliability problems. As much as 80–90% of the ash is impacted on the burner of a cyclone fired furnace [45]. A large fraction of the ash, 60–100%, leaves the combustion chambers of most other types of boilers with the flue gases.

After the combustion products leave the combustion chamber, they enter a series of heat exchangers where heat is transferred from the hot gases to the heat transfer surfaces primarily by convection. In this region the combustion products are cooled from the boiler outlet temperature to the inlet temperature of the emission control equipment, 300–700°K, in a residence time of several seconds. The formation of deposits in this region and the corrosion that accompanies the deposits are major causes of boiler failure. The fraction of the ash deposited in this region is probably small.

4. MINERAL MATTER IN COAL

The ash forming constituents of coal occur in two main classes. Inherent mineral matter, which seldom exceeds 2% of the coal mass, is derived from the original plant substance. Extraneous mineral matter is inorganic material that was mixed with the plant substance as the coal was formed or during mining operations [37].

The extraneous mineral matter may be present as very fine inclusions dispersed throughout the coal volume, or it may be made up of large, distinct structures. The mineral inclusions are generally small compared to the mean coal particle size. Padia [33] has reported Rosin–Rammler distributions fit to mineral size distributions measured after the carbon matrix of coal was oxidized in a low temperature ($T\approx425$°K) oxygen plasma. The measured volume mean diameters were 1.7 and 2 μm for a

lignite and a bituminous coal, respectively. From the size distribution parameters reported, the number mean diameter of the lignite inclusions is about 1 μm. It is not possible to determine the number mean diameter using the parameters given for the inclusions in the bituminous coal.

The mineral matter in coal consists primarily of kaolinite ($Al_2O_3\cdot2SiO_2\cdot2H_2O$), pyrites ($FeS_2$), and calcite ($CaCO_3$) [37, 46]. The major elements in the coal minerals are those found in silicate rocks, silicon, aluminum, calcium, magnesium, iron, sulfur, sodium, potassium, chlorine, and titanium [47]. The mean concentrations of these major elements and a number of minor and trace species in coal are presented in Table 1.

Table 1. MEAN COMPOSITION FOR 101 COALS[a]

Constituent[b]	Mean		Standard Deviation	Min	Max
As	14.02	PPM	17.70	0.50	93.00
B	102.21	PPM	54.65	5.00	224.00
Be	1.61	PPM	0.82	0.20	4.00
Br	15.42	PPM	5.92	4.00	52.00
Cd	2.52	PPM	7.60	0.10	65.00
Co	9.57	PPM	7.26	1.00	43.00
Cr	13.75	PPM	7.26	4.00	54.00
Cu	15.16	PPM	8.12	5.00	61.00
F	60.94	PPM	20.99	25.00	143.00
Ga	3.12	PPM	1.06	1.10	7.50
Ge	6.59	PPM	6.71	1.00	43.00
Hg	0.20	PPM	0.20	0.02	1.60
Mn	49.40	PPM	40.15	6.00	181.00
Mo	7.54	PPM	5.96	1.00	30.00
Ni	21.07	PPM	12.35	3.00	80.00
P	71.10	PPM	72.81	5.00	400.00
Pb	34.78	PPM	43.69	4.00	218.00
Sb	1.26	PPM	1.32	0.20	8.90
Se	2.08	PPM	1.10	0.45	7.70
Sn	4.79	PPM	6.15	1.00	51.00
V	32.71	PPM	12.03	11.00	78.00
Zn	272.29	PPM	694.23	6.00	5350.00
Zr	72.46	PPM	57.78	8.00	133.00
Al	1.29	%	0.45	0.43	3.04
Ca	0.77	%	0.55	0.05	2.67
Cl	0.14	%	0.14	0.01	0.54
Fe	1.92	%	0.79	0.34	4.32
K	0.16	%	0.06	0.02	0.43
Mg	0.05	%	0.04	0.01	0.25

Table 1. (Continued)

Constituent[b]	Mean		Standard Deviation	Min	Max
Na	0.05	%	0.04	0.00	0.20
Si	2.49	%	0.80	0.58	6.09
Ti	0.07	%	0.02	0.02	0.15
ORS	1.41	%	0.65	0.31	3.09
PYS	1.76	%	0.86	0.06	3.78
SUS	0.10	%	0.19	0.01	1.06
TOX	3.27	%	1.35	0.42	6.47
SXRF	2.91	%	1.24	0.54	5.40
ADL	7.70	%	3.47	1.40	16.70
MOIS	9.05	%	5.05	0.01	20.70
VOL	39.70	%	4.27	18.90	52.70
FIXC	48.82	%	4.95	34.60	65.40
ASH	11.44	%	2.89	2.20	25.80
BTU/LB	12748.91		464.50	11562.00	14362.00
C	70.28	%	3.87	55.23	80.14
H	4.95	%	0.31	4.03	5.79
N	1.30	%	0.22	0.78	1.84
O	8.68	%	2.44	4.15	16.03
HTA	11.41	%	2.95	3.28	25.85
LTA	15.28	%	4.04	3.82	31.70

[a]From Ref. 47, reprinted with permission.

[b]Abbreviations other than standard chemical symbols: organic sufur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high temperature ash (HTA), low temperature ash (LTA).

When coal is heated, the mineral matter undergoes a number of transitions [48]. At temperatures below about 500°K dehydration and changes in mineral forms occur. Pyrite is oxidized at temperatures below about 800°K. Carbonates and sulfates decompose at temperatures in the range 500–1100°K, evolving CO_2, SO_2, and SO_3. Alkali salts, such as chlorides, are volatilized at an appreciable rate when the temperature exceeds about 1350°K. Silica may volatilize at temperatures higher than about 1900°K [33, 35, 36, 49–54], largely because of the reduction of SiO_2 by reaction with carbon to form SiO, which is much more volatile than SiO_2. At temperatures higher than about 2500°K, a condition that is not achieved in conventional pulverized coal combustion but may occur in magnetohydrodynamic generators, appreciable quantities of alumina may also be volatilized. Measurements of the distribution of ash composition as a function of

particle size suggest that many minor ash constituents are also vaporized during coal combustion.

The tests that determine the ash content of coals involve the slow combustion of coal at a relatively low temperature, about 1000°K, and determination of the quantity of the residual ash. Since combustion in boilers occurs at much higher temperatures, transitions that do not occur in the standard tests may take place. Some of these changes result in the evolution of considerable quantities of CO_2, SO_2, and SO_3. This decomposition may account for a major fraction of the weight loss of the ash, as is shown in Fig. 3. Nonetheless, a substantial fraction of the ash may be lost through vaporization. As much as 4–8% of the ash was vaporized in Padia's experiments [33].

The tendency of ash to melt when heated has posed problems for engineers since the earliest days of steam generation [37]. When coal is

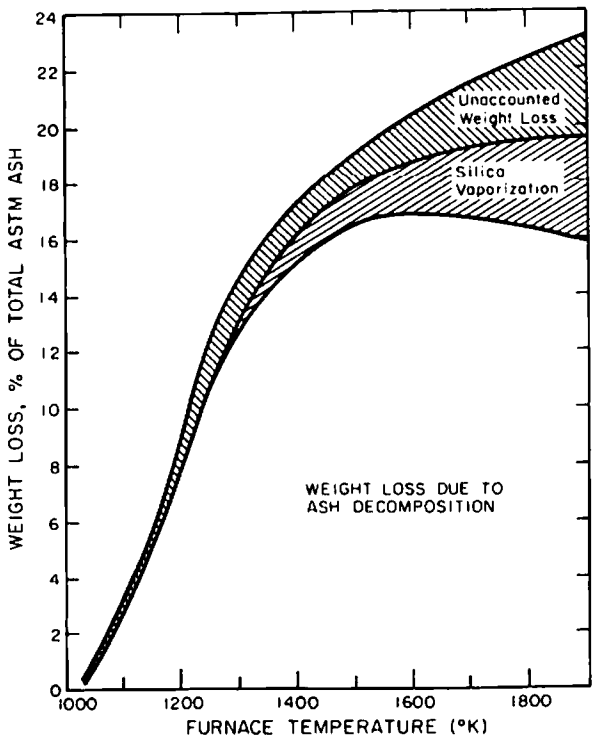

Fig. 3. Loss of ash during fuel lean combustion of 38–45 μm lignite particles in a laminar flow furnace. (From Ref. 33.)

burned in a fuel bed, the ash softens and then may fuse to form clinkers. To determine the relative tendencies of different coals to form clinkers, tests were devised to measure the fusibility of ash. Empirical tests have been developed to determine the initial deformation temperature, the softening temperature, and the fluid temperature [37]. More quantitative information is obtained for some ashes by measuring the viscosity of the ash as a function of temperature. The viscosity of the ash decreases rapidly with increasing temperature and also depends strongly on the composition of the ash. The presence of iron as Fe_2O_3 in the ash results in the ash behaving as a fluid at much lower temperatures than the same ash would behave if the iron were present only in its reduced state, FeO [37]. Other species have similar strong effects on the characteristics.

Examination of fly ash particles reveals that most particles were molten during their formation process. The particles tend to be spherical except where considerable agglomeration has occurred. Since the temperature at which the ash becomes fluid may vary over several hundred degrees, depending on the coal characteristics and whether the combustion environment is oxidizing or reducing, and since the peak temperatures are determined by the combustion conditions, it is expected that combustion conditions may strongly influence the character of the ash emissions.

5. FLY ASH PARTICLE FORMATION

The processes that influence the ash particle formation occur primarily in the final stages of coal particle burnout. Initially, as a coal particle is heated, volatile hydrocarbons originally present in the coal or produced by pyrolysis are vaporized. Some of the mineral matter inherent in the organic structure of the coal may be vaporized during this process. Mercury and other extremely volatile ash constituents may also be vaporized during this early phase of combustion. After the volatile hydrocarbons are vaporized, the residual char burns by heterogeneous oxidation, both on the external surface of the coal particle and internally. Under some conditions a coal particle may burn with very little change in diameter, the particle density decreasing because of internal burning. The rate at which coal particles smaller than about 100 μm burn is, at temperatures below about 2000–2500°K, controlled by chemical kinetic processes. Diffusion of oxygen to the particle surface limits the rate of combustion of larger particles.

On heating, coal swells and becomes hollow or porous [28, 32, 55–59]. The degree of swelling depends on both the coal type and the combustion conditions. Hollow char particles, known as cenospheres, may be formed, particularly if the heating takes place in a reducing atmosphere [55].

Porous vesicular particles are more likely to form if the heating occurs in an oxidizing environment. Coal particles burn on both external and internal surfaces, so as a particle burns, fragile, lacy char structures are formed that eventually disintegrate [28, 56–59].

Ramsden [28] has postulated that mineral inclusions in coal particles melt within the carbon lattice as the combustion front approaches. Water vapor, carbon dioxide, and other gases are evolved because of the temperature rise. If the heating occurs sufficiently rapidly, the sudden increase in pressure within an inclusion and the decrease in the ash viscosity may shatter the inclusion, dispersing the ash into minute droplets. This dispersal may be accompanied by the disintegration of the carbon framework, releasing submicron particles into the gas stream, or the droplets may remain within the carbon framework and coalesce into a liquid layer. The ash has very high surface tension and does not wet the carbon surface. Therefore as the receding carbon surface brings molten inclusions into contact, the ash may coalesce to form spherical droplets larger than the original mineral inclusions. If the temperature of the particle is below the fusion point, the ash inclusions will not coalesce but may agglomerate and, if the temperature is not too low, sinter to form irregularly shaped ash particles. Hollow spherical fly ash particles, known as cenospheres, may form if gas evolution occurs within the particles at temperatures sufficiently high ($T \gtrsim 1200$°K) for the ash to be fluid but low enough ($T \lesssim 1500$°K) that the viscosity prevents the particles from expanding so rapidly that they burst [26, 33, 34]. Cenospheres are usually large ($d_p \gtrsim 50$ μm) and, in large furnaces, account for no more than a few percent of the fly ash mass [26]. Fly ash particles containing bubbles have also been observed [24]. These particles may be formed at temperatures too low to result in cenosphere formation. Cenospheres that contain fly ash or char particles, called plerospheres [34], are probably formed from these particles.

Only a few of these processes need be considered to describe the formation of the dense fly ash particles that account for most of the mass of the particulate matter produced. These processes are summarized in Fig. 4. As a coal particle burns, the mineral inclusions melt and, when the receding carbon surface brings them into contact with one another, coalesce. Because of internal burning, the char particle may break up into a number of fragments. Thus more than one ash particle may be produced from each coal particle, but the total number of ash particles produced may be much less than the total number of mineral inclusions in the coal particle.

Laboratory experiments in which size segregated coal samples were burned in a laminar flow furnace have demonstrated the relationship

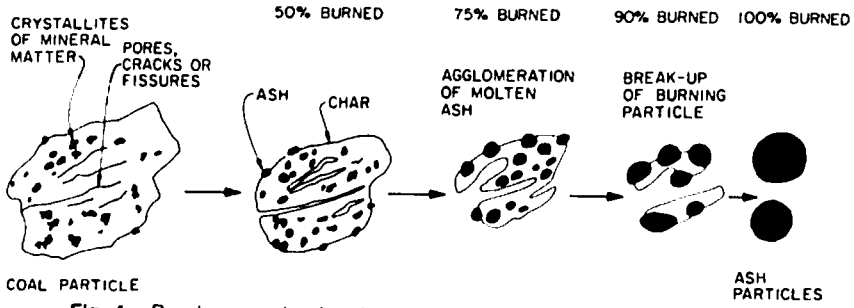

Fig. 4. Breakup mechanism for the formation of large fly ash particles.

between the coal particle size distribution and the size of large, dense ash particles produced during combustion [33]. Two size cuts, 38–45 μm and 75–90 μm, of two coals, a Pennsylvania bituminous coal and a Montana lignite, were burned under nearly constant temperature conditions. The swelling bituminous coal formed more cenospheres than did the relatively nonswelling lignite. Cenospheres were removed from the ash samples by density segregation in water. The ash particles denser than water were then sized by electron microscopy. Because of the sampling system, which used water to cool the ash, the density segregation system, and the large numbers of particles collected on the electron microscope grids, only particles larger than a few microns in diameter could be counted reliably. The measured size distribution of the ash particles could be correlated with the coal particle size by assuming that three ash particles per lignite particle and about five ash particles per bituminous coal particle were produced during combustion. These numbers are consistent with the expectation that the highly porous char particles formed by the highly swelling bituminous coal would break up into a larger number of fragments than the relatively nonswelling lignite. The number of ash particles produced per coal particle did not vary significantly over a factor of 2 change in the coal particle size.

Application of this breakup model to the formation of large fly ash particles in coal fired combusters requires knowledge of the coal particle size distribution, the ash forming characteristics of the coal being burned, and the combustion conditions. These data are not available for any studies in which the ash particle size distributions were also measured. Most measurements of coal particle size distributions have been made by mechanical sieving of the coal and provide little information about particles smaller than 50 μm. Measurements made using aerodynamic sizing and microscopy provide some data on the quantities of particles as small as a few microns in diameter, but the data are limited. Littlejohn [41]

measured the size distribution of pulverized coal as supplied to the burners in a number of boilers. The coal particle size distribution varied considerably from one installation to another. The ash content was also found to vary with coal particle size as a result of the design of pulverizers. The pulverized coal is removed from the mills aerodynamically. Since the mineral density, 2–6 g cm^{-3}, is higher than the coal density, about 1.3 g cm^{-3}, particles that contain significant quantities of mineral matter tend to remain in the pulverizers longer than do particles with a lower mineral content. The finest particles measured by Littlejohn, of about 14 μm diameter, included many consisting entirely of mineral matter and had a mean ash content as much as two times higher than the bulk of the coal.

In spite of these complications, we use these data to test the breakup model for ash formation. For the present purposes we assume that the mineral matter is uniformly distributed through all the coal particles and that p equal mass ash particles are produced from each coal particle. We further assume that the number of ash particles produced is independent of the coal particle size and the density of the ash particles is constant. If the mass fraction of ash in the coal is α (typically 5–20%), a coal particle of mass m produces p particles of mass $m = \alpha m'/p$. Noting that the ash density ρ_a is greater than the coal density ρ_c, the volume of the ash particles produced is

$$v = \frac{\alpha_v v'}{p} \tag{1}$$

where

$$\alpha_v = \alpha\left(\frac{\rho_c}{\rho_a}\right) \tag{2}$$

If the coal particle size distribution is $n_c(d_c)$, the ash particle size distribution is

$$n(d_p) = p\left(\frac{p}{\alpha_v}\right)^{1/3} n_c\left(d_p\left(\frac{p}{\alpha_v}\right)^{1/3}\right) \tag{3}$$

It is unlikely that the burnout of coal particles will result in the formation of ash particles smaller than the original mineral inclusions. For this reason the predicted ash size distribution has been truncated at the particle size where the ash particles predicted by the breakup model are the same size as the mass mean inclusion size. Below this size the coal particles are not expected to contain enough separate mineral grains to produce more than one ash particle per coal particle. These fine ash particles are assumed

to have the same size distribution as the mineral inclusions in the coal and to be unaffected by the coal particle size.

These calculations are compared in Fig. 5 with the mass size distribution data of McCain et al. [1], normalized with respect to the total mass of aerosol expected from a coal containing 10% ash burned at a fuel–air equivalence ratio of 0.85, that is, 15% excess air, with no loss of ash to the boiler walls. The data (solid points) are the averages of the measurements obtained at the electrostatic precipitator inlets of six pulverized coal fired power plants. The curve is the prediction of the breakup model assuming that the coal contains 10% ash and that the coal and ash densities are 1.3 and 2.3 g cm^{-3}, respectively, and using a Rosin–Rammler mass distribution, which Field [40] suggests is typical for pulverized coal:

$$dM/d(d_p) = \left(\frac{1.2M}{d_p}\right)\left(\frac{d_p}{53\mu m}\right)^{1.2} \exp\left(-\left(\frac{d_p}{53\mu m}\right)^{1.2}\right) \qquad (4)$$

where M is the total mass of coal per unit volume. It is assumed in this calculation that $p=4$. The coal size data of Littlejohn [41] are used to illustrate the sensitivity of the ash particle size distribution to the value of p

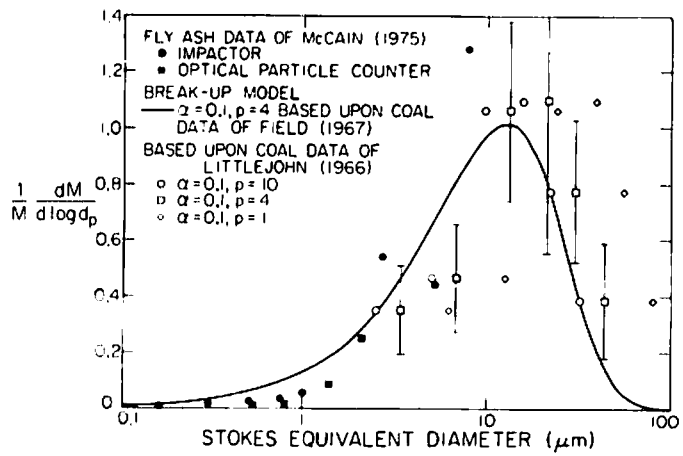

Fig. 5. Comparison of the mass distribution calculated using the breakup model with the fly ash size distribution measured upstream of electrical precipitators on coal fired power plants. The error bars on the $p=4$ points indicate the standard deviation in the calculated size distribution that results from the highly variable coal particle size distribution data of Littlejohn [41].

points. Values of $p=1$ (diamonds), $p=4$ (squares), and $p=10$ (circles) are illustrated. In spite of the large uncertainty in the coal size data and the use of coal size data and breakup model parameters derived in systems different from those in which the measurements were made, the calculations are in qualitative agreement with the data. Part of the discrepancy may be due to the arbitrary parameters used to estimate the total mass loading used in normalizing the fly ash data. The available coal size data permit predictions of ash size distributions only for particles larger than a few microns in diameter.

The fly ash number size distribution provides more information about the submicron particles. McCain et al. [1] have measured the distribution of submicron fly ash particles by using a combination of particle sizing

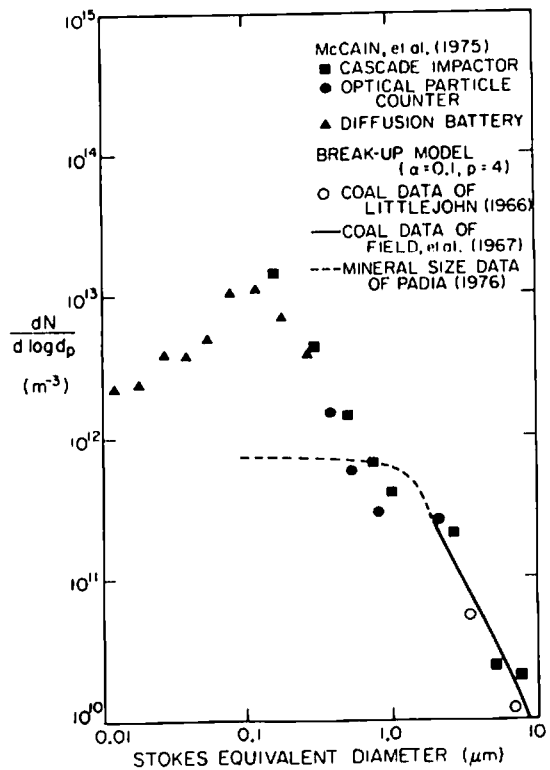

Fig. 6. Comparison of the number distribution predicted using the breakup model with the data of McCain et al. [1].

techniques, including a cascade impactor, an optical particle counter, and a diffusion battery. These data are presented in Fig. 6. The predictions of the breakup model for fly ash particle formation were made assuming $p=4$ and using the assumptions described earlier for ash constant and combustion conditions. The solid line is the prediction made using the coal size distribution of Field [40] and the open points are based on the data of Littlejohn [41]. The broken line shows the effect of truncating the size distribution with mineral size data obtained by Padia [33] for bituminous coal. The total number of particles predicted by this model is much less than the number measured by McCain et al. [1]. It does, however, show very close agreement with the measured numbers of particles larger than about 1 μm diameter. The discrepancy between the theory and the data below 1 μm is sufficiently large that minor changes in the parameters used in the calculations do not account for the difference.

6. FINE PARTICLE FORMATION

The simple breakup model predicts the size distribution of fly ash particles larger than the mineral inclusions. The calculated size distribution is in reasonable agreement with the measured volume distribution of fly ash, but does not agree with the measured number distribution for particles smaller than about 1 μm diameter. A mechanism that can produce several fly ash particles from a single mineral inclusion is required to explain the formation of large numbers of fine particles.

Two mechanisms of fine particle production have been identified. Gas evolution inside molten ash particles forms bubbles that may burst, breaking a single molten ash particle into a number of fine droplets [28]. The size of particles produced by this mechanism is not known, but will certainly depend on the ash composition and temperature, both of which strongly influence the viscosity of the ash [37]. Measurements of the contribution of this mechanism to fine particle formation are required before the breakup model can be extended to include this process. Some ash constituents vaporize in the flame. As the combustion products cool or when the chemical form of the volatilized ash changes (e.g., oxidation of SiO to form the less volatile species, SiO_2), the ash may condense. In spite of the high number densities produced by the breakup mechanism, some of the vapor may condense homogeneously to form very fine particles. Soot particles that are about 0.03–0.1 μm in diameter are formed in this manner [22, 23, 28], and there have been observations of production of a very fine silica aerosol, 0.01–0.15 μm in diameter, during coal combustion [35, 36]. The quantity of ash formed by homogeneous nucleation is not known. Homogeneous nucleation can produce finer particles than would be expected by any mechanical breakup process. With the limited data available

the relative importance of the two mechanisms for fine particle formation cannot be evaluated.

The quantity of ash in the submicron size range is only a small fraction, 0.5–4% [1], of the total mass produced during combustion. Condensation of volatilized ash could, based on available data, form this mass of submicron sized particles. Silica accounting for as much as 4% of the ash was vaporized in laminar flow furnace experiments [33]. Another 4% ash loss that was not explained by ash decomposition may be the result of ash vaporization (see Fig. 3). Although these data were not obtained in large pulverized coal combustors, they do suggest that ash vaporization could result in the formation of a quantity of fine fly ash comparable to the measured mass of submicron particles. In the following analysis the contribution of homogeneous nucleation to fine particle production is explored qualitatively by assuming that a small fraction of the ash vaporizes during combustion.

Vaporization of 1% of the ash produces about 0.1 g of condensible material per standard cubic meter. Homogeneous nucleation of this ash would yield a very large number of extremely small particles, probably much smaller than 0.01 μm in diameter. These particles may coagulate with other particles produced by homogeneous nucleation, or they may diffuse to the surfaces of the much larger particles produced by the breakup process. In addition, heterogeneous condensation may occur after homogeneous nucleation. These processes reduce the number of particles produced by condensation and increase their average size.

As long as the particles are much smaller than the mean free path of the gas molecules, the evolution of the aerosol produced by homogeneous nucleation may be described by the theory of self-preserving size distributions for the free molecule regime [60, 61]. Previous applications of this theory have dealt with aerosol evolution in constant density systems. Since the temperature in combustion systems may change over nearly an order of magnitude, the analysis of Lai et al. [60] must be modified to treat variable density flows. For a fluid with uniform composition, the kinetic equation for aerosol evolution is [62]

$$\frac{\partial n(v,t)}{\partial t} + \nabla \cdot n(v,t)\mathbf{u} = \frac{1}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v}) n(\tilde{v},t) n(v-\tilde{v},t)\, d\tilde{v} - \int_0^\infty \beta(v,\tilde{v}) n(v,t) n(\tilde{v},t)\, d\tilde{v} \tag{5}$$

where v is the particle volume, $\mathbf{u}$ the gas velocity, and β the collision

frequency function. It is convenient to write the aerosol size distribution in terms of unit mass of carrier fluid instead of volume, that is,

$$\tilde{n}(v,t) = \frac{n(v,t)}{\rho} \tag{6}$$

Substituting Eq. 6 into Eq. 5 and using conservation of mass, the result is

$$\rho\frac{\partial \tilde{n}(v,t)}{\partial t} + \rho\mathbf{u}\cdot\nabla\,\tilde{n}(v,t)$$

$$= \frac{\rho^2}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v})\tilde{n}(\tilde{v},t)\tilde{n}(v-\tilde{v},t)\,d\tilde{v}$$

$$-\rho^2\int_0^\infty \beta(v,\tilde{v})\tilde{n}(v,t)\tilde{n}(\tilde{v},t)\,d\tilde{v} \tag{7}$$

The left-hand side represents the substantial derivative

$$\rho\frac{d\tilde{n}}{dt} = \rho\frac{\partial\tilde{n}}{\partial t} + \rho\mathbf{u}\cdot\nabla\,\tilde{n}$$

The right-hand side represents the usual coagulation terms written in terms of number per unit mass. The total number and volume of particles may also be calculated on a mass basis, namely,

$$\tilde{N}_s = \int_0^\infty \tilde{n}(v,t)\,dv$$

$$\tilde{V}_s = \int_0^\infty v\tilde{n}(v,t)\,dv \tag{8}$$

Following the analysis of Lai et al. [60], we find that the total number of fine particles decays according to

$$\frac{dN_s}{dt} = -\frac{1}{2}\left[\frac{3}{4\pi}\right]^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{P}{RT}\right)I_1\tilde{V}_s^{1/6}\tilde{N}_s^{11/6} \tag{9}$$

where $I_1 = 6.67$ [60] is the dimensionless collision integral. From this result we see that the rate of loss of particles due to coagulation varies inversely with the $1/2$ power of the temperature.

The number and size of the fine particles also change by diffusion of fine particles to larger particles and heterogeneous condensation. The self-preserving theory is a reasonable approximation for the evolution of

the fine aerosol if the rate of loss of fine particles to the surfaces of larger particles is slow compared to the rate of coagulation and the rate of particle growth by condensation is small compared to the growth by coagulation. The number of particles of size d_s to $d_s + d(d_s)$ diffusing to the surface of a large particle of size d_L per unit time is

$$F = \frac{2\pi D(1+\mathrm{Kn}_L)\tilde{n}_s(d_s)d(d_s)}{(1+1.71\mathrm{Kn}_L+1.333\mathrm{Kn}_L^2)} \tag{10}$$

where $\mathrm{Kn}_L = 2\lambda/d_L$ is the Knudsen number and the Fuchs and Sutugin interpolation formula [63] has been used to describe the diffusion of particles in the transition regime. The total rate of loss of small particles to all large particles is

$$\left(\frac{d\tilde{N}_s}{dt}\right)_D = \frac{-I_D I_2(2\pi mkT)^{1/2}\tilde{N}_s^{5/3}\tilde{V}_s^{-2/3}}{\left(\frac{2}{3}\right)(1+\pi\alpha_c/8)(6/\pi)^{2/3}} \tag{11}$$

The diffusion integral is defined as

$$I_D = \int_{d_L}\frac{(1+\mathrm{Kn}_L)d_L\tilde{n}_L(d_L)d(d_L)}{(1+1.71\mathrm{Kn}_L+1.333\,\mathrm{Kn}_L^2)} \tag{12}$$

and is a function of temperature since $\lambda \propto T$. The integral

$$I_2 = \int_0^\infty \psi(\eta)\eta^{-2/3}\,d\eta \tag{13}$$

has a value of 1.87. Thus total rate of decay of the number of particles is the sum of Eqs. 9 and 11, that is,

$$\frac{d\tilde{N}_s}{dt} = -\left(\frac{I_1}{2}\right)\left[\frac{3}{4\pi}\right]^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{P}{RT}\right)\tilde{V}_s^{1/6}\tilde{N}_s^{11/6}$$

$$-\frac{I_D I_2(2\pi mkT)^{1/2}\tilde{N}_s^{5/3}\tilde{V}_s^{-2/3}}{\left[\left(\frac{2}{3}\right)(1+\pi\alpha_c/8)(6/\pi)^{2/3}\right]} \tag{14}$$

It is important to note that this equation is valid only if the magnitude of the second term is much smaller than that of the first term.

The volume of small particles also decreases as a result of diffusion to the surface of large particles. The rate of decay of the volume of fine

particles is

$$\frac{d\tilde{V}_s}{dt} = \frac{-I_D I_3 \left(\frac{3}{2}\right)(2\pi mkT)^{1/2}(\pi/6)^{2/3}\tilde{N}_s^{2/3}\tilde{V}_s^{1/3}}{(1+\pi\alpha_c/8)} \tag{15}$$

where

$$I_3 = \int_0^\infty \eta^{1/3}\psi(\eta)\,d\eta = 0.885 \tag{16}$$

This model for the evolution of the size distribution has been used to examine the contribution of homogeneous nucleation to the formation of submicron ash particles. Several important assumptions were made. The large particle size distribution given by the breakup model was assumed to be unaffected by coagulation or by diffusion of fine particles to the surfaces of the large particles. This assumption is reasonable for particles larger than 1 μm but may not be appropriate for smaller particles. The furnace, illustrated in Fig. 2, is modeled as a plug flow reactor with uniform composition and temperature at any point. The temperature is assumed to remain constant at a flame temperature of 1800°K for 0.5 sec. The temperature of the combustion products then decreases at a constant rate to the furnace outlet temperature, 1400°K, in 1 sec. Once the combustion products enter the convective heat exchangers, heat transfer is more rapid; the temperature decreases to 425°K in 2 sec. It was further assumed that 1% of the fly ash was vaporized during combustion and immediately condensed by homogeneous nucleation.

The fly ash size distribution calculated using this model is shown in Fig. 7. The total number of particles predicted is an order of magnitude greater than the measured value, and the calculated size distribution has a narrow peak at a particle diameter of about one-fifth that of the broader peak of the measured distribution. Although the predicted small particle number concentration is too large, we estimate that only one-fourth of the fine particle volume is lost by diffusion to the surfaces of the larger particles. We can, therefore, neglect the second term of Eq. 14 in the examination of the causes of this large discrepancy.

The total number of particles is obtained by integrating Eq. 9 with the assumption that the number initially is infinite:

$$\tilde{N}_s = \left(\tfrac{5}{6}K\tilde{V}_s^{1/6}\tau\right)^{-6/5} \tag{17}$$

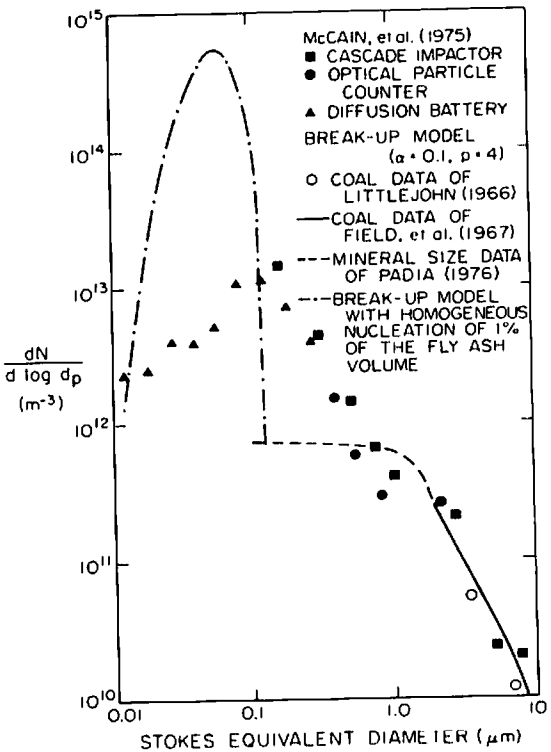

Fig. 7. Comparison of the number distribution calculated using the breakup model with homogeneous nucleation of 1% of the ash with the measured size distribution.

where

$$K = \left(\frac{I_1}{2}\right)\left[\frac{3}{(4\pi)}\right]^{1/6}\left(\frac{6kT_0}{\rho_p}\right)^{1/2}\left(\frac{P}{RT_0}\right)$$

$$\tau = \int_0^t \sqrt{T_0/T}\,dt \tag{18}$$

and T_0 is an arbitrary reference temperature. The total number of particles is proportional to $\tau^{-6/5}$. Even with this strong dependence on the residence time, increase in the residence time alone cannot account for all the discrepancy. The residence time would have to be increased by about a factor of 30 to bring the calculations into reasonable agreement with the

measurements. Such a factor would not be reasonable for the usual combustion conditions.

Interparticle dispersion forces increase the rate of coagulation of aerosols in the free molecule regime by a factor that depends on the sizes of the colliding particles and the ratio $A/(kT)$ [61]. The Hamaker constant A depends on the nature of the two interacting materials. Graham and Homer [61] have estimated the effect of dispersion aerosols on the coagulation of a free molecular aerosol of lead with a self-preserving size distribution. The coagulation rate increased by a factor of 2 for a value of $A/(kT)=15$ and a factor of 2.5 for $A/(kT)=39$. The Hamaker constant of silica is $6-12\times10^{-13}$ erg [64, 65]. The ratio A/kT is in the range 1.7–30 for a silica aerosol in a combustion system. Based on the calculation of Graham and Homer [61], we estimate that the coagulation rate increases by less than a factor of 2.5. Thus dispersion forces may reduce the total number of particles by as much as a factor of 3, but cannot account for the full difference between the measured and calculated number of particles.

The number of ash particles depends only weakly on the volume of ash in the fine particle mode,

$$\tilde{N}_s \propto \tilde{V}_s^{-1/5} \tag{19}$$

however, the size of the particles produced is a somewhat stronger function

$$d_s = \left(\frac{6}{\pi}\cdot\frac{\tilde{V}_s}{\tilde{N}_s}\right)^{1/3} \propto \tilde{V}_s^{2/5} \tag{20}$$

Thus an increase in the concentration of the condensing species would reduce the number and increase the size of the particles produced by homogeneous nucleation. A large change in concentration is required to produce a significant change in the aerosol characteristics.

The composition of the gas in a flame is highly nonuniform. Although a furnace is supplied with excess air, regions of the combustion zone have greater than the stoichiometric fuel–air ratio. Spatial variations in composition occur in the regions of fuel and air injection, and some spatial inhomogeneity may persist throughout the flow. Localized fluctuations in composition that are dissipated by turbulence are also important to aerosol evolution. Corrsin [66] has shown that second order kinetic processes, such as aerosol coagulation, are accelerated by these small scale fluctuations in composition.

Several processes not considered in the model may have major influence on the particle size distribution. Heterogeneous condensation may increase the size of the fine particles. Highly volatile ash constituents may condense

after large numbers of particles have been produced by the homogeneous nucleation of less volatile species. Because of the very large surface area of the fine particles, the more volatile compounds may condense on existing particles. Species other than ash may also condense on the fine particles. Sulfur trioxide and water vapor are both present in the combustion products. As the combustion products cool, these two species may react to form sulfuric acid and condense.

Some of the fine particles are soot rather than fly ash. The quantity of soot produced during coal combustion is not known. Soot is formed by the condensation and subsequent pyrolysis of high molecular weight hydrocarbons [22]. These soot precursors are formed only in very fuel-rich regions of flames. The soot particles burn readily in the presence of oxygen at combustion temperatures but burn very slowly at lower temperatures [67]. Relatively minor changes in combustion conditions may result in substantial changes in the quantity of soot produced. In a recent study, combustion modifications designed to reduce emissions of oxides of nitrogen resulted in a factor of 5 increase in the number of particles in the range 0.01–0.1 μm diameter [20], the typical size range for soot particles.

Until the chemical composition of the submicron particles is known, we can only speculate about the relative importance of ash, sulfates, and soot. The contributions of these components may vary significantly from one combustor to another. The formation of fine ash and soot particles is dependent on combustion conditions. Sulfates may be present as either gases or particles, depending on the flue gas temperature at the point where the sample is taken.

Finally, the discrepancy between the model calculations and the measured number of submicron particles may be attributed in part to uncertainties in the experimental measurements. Even diluting the sample by a ratio of 1000:1, the number concentration of particles measured is sufficiently high (initially 10^{13} m^{-3} measured and 2×10^{14} m^{-3} calculated) that either the diffusion battery-condensation nuclei counter system [1] or the electrical aerosol analyzer [20] might not be able to count all the particles. Moreover, neither of the two instruments has perfect size resolution, so it is expected that the measured peak in the number distribution would be somewhat broader than the actual distribution.

7. FINE PARTICLE ENRICHMENT BY VOLATILE SPECIES

A number of ash species vaporize during combustion and later condense either homogeneously or heterogeneously. Homogeneous nucleation produces very fine particles containing the volatile ash species. Heterogeneous condensation may also concentrate volatile species in fine particles. The

number of molecules of condensing species condensing per unit time on the surface of a particle of size d_p (number per second) in the free molecule regime ($Kn > 1$) is

$$F_i = \alpha_c \pi d_p^2 \left(\frac{kT}{2\pi m_i} \right)^{1/2} (C_i - C_{i,s}) \tag{21}$$

where C_i is the concentration in molecules per unit volume and $C_{i,s}$ is the saturation concentration. The number of molecules condensing on particles of size d_p per unit mass of particles is

$$\frac{F_i}{[\rho_p(\pi/6)d_p^3]} \propto d_p^{-1} \tag{22}$$

Thus the concentration of a condensing species on particles in the free molecule regime is expected to be inversely proportional to the particle diameter.

In the continuum regime, $Kn < 1$, the number of particles and the number of molecules condensing per unit time on a particle is

$$F_i = 2\pi d_p D(C_i - C_{i,s}) \tag{23}$$

Thus the number of molecules of the condensed species per unit mass of particles is inversely proportional to the square of the particle diameter, for example,

$$\frac{F_i}{[\rho_p(\pi/6)d_p^3]} \propto d_p^{-2} \tag{24}$$

Composition–size distribution data are available for a number of fly ash species in particles larger than about 1 μm diameter, that is, the continuum size range even at the highest temperatures in a furnace [11–17]. Davison et al. [11] have shown that the concentrations of several volatile ash constituents were well correlated with the particle size by the expression,

$$\bar{C} = C_0 + \frac{6C_s}{\rho_p d_p} \tag{25}$$

which is consistent with adsorption on the particle surface. The data are also well correlated by Eq. 24 as is shown in Fig. 8. The correlations of the concentrations of the species that exhibited the most pronounced increase

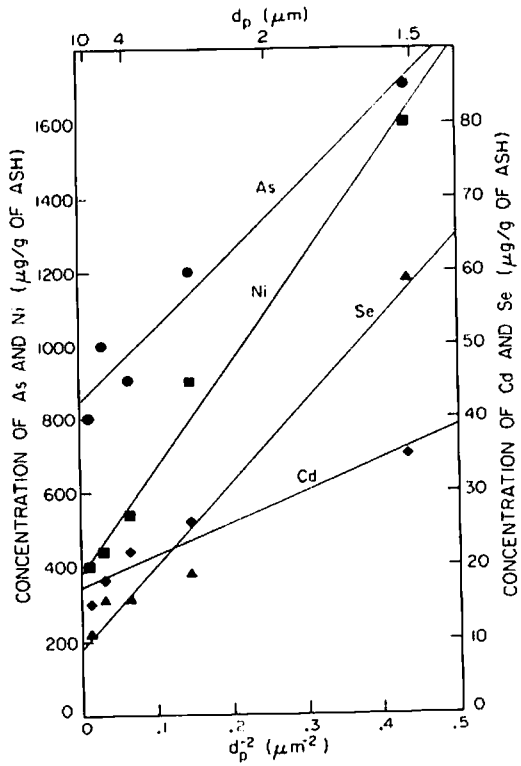

Fig. 8. Dependence of element concentration on particle size fly ash emitted from a coal fired power plant [11].

in concentration with decreasing particle size are summarized in Table 2. The linear correlation coefficients calculated using both models are comparable for all species considered. These data are not sufficient to differentiate between condensation and adsorption. Sulfur is present in fine fly ash particles in concentrations too large to be explained by adsorption alone, so it appears that some species do condense [11]. The existence of a surface layer containing high concentrations of volatile ash species has recently been confirmed by ion microprobe studies on large fly ash particles [68].

There are few data on the composition–size distribution for submicron fly ash particles. Ragaini and Ondov [16] observed two peaks in the number distribution, a sharp peak occurring at about 0.1 μm diameter and a second peak at about 1 μm. A number of species were found in the

Table 2. PARAMETERS DERIVED FROM SURFACE DEPOSITION MODELS

	Present Work			Davidson et al. [11]			
		$c = a + b/d_p^2$	Linear		$c = C_0 + 6C_s/(\rho_p d_p)$		Linear
Element	a ($\mu g g^{-1}$)	b ($\mu g \cdot \mu m^2 g^{-1}$)	Correlation Coefficient	C_0 ($\mu g cm^{-2}$)	C_s ($\mu g g^{-1}$)		Correlation Coefficient
Pb	1400	530	0.58	0.04	1000		0.73
Tl	55	53	0.71	0.003	40		0.80
Sb	30	54	0.97	0.007	20		0.93
Cd	17	43	0.96	0.002	10		0.99
Se	9	110	0.98	0.004	0.7		0.92
As	850	2000	0.98	0.009	600		0.97
Zn	7400	16000	0.59	0.6	6000		0.60
Ni	770	2900	0.99	0.1	100		0.98
Cr	220	7200	0.99	0.3	300		0.94

smaller peak in much higher concentrations than in the larger peak. The data are only qualitative, however, since neither the total mass loading of the collected aerosol nor the quantities of particles larger than about 3 μm were reported.

The condensation of a volatile species onto the submicron ash can be explored by a simple calculation. The rate of condensation onto particles over the entire range of particle sizes can be described by using the Fuchs and Sutugin interpolation formula [63], for example,

$$F_i = \frac{2d_p D_i (1 + K_n)}{(1 + 1.71K_n + 1.333K_n^2)(C_i - C_{i,s})} \tag{26}$$

The total deposition rate (molecules sec^{-1} g^{-1}) of a species condensing at a temperature T on an aerosol with a size distribution $\tilde{n}(d_p, t)$ is

$$f_i(d_p, T) = \int_0^\infty F_i(d_p, T)\tilde{n}(d_p, t)d(d_p) \tag{27}$$

The calculated condensation rate distribution of a species condensing on particles with the size distribution measured by McCain et al. [1] is shown in Fig. 9.

This result suggests that the majority of a species condensing at this temperature would be concentrated in the submicron particles. If the

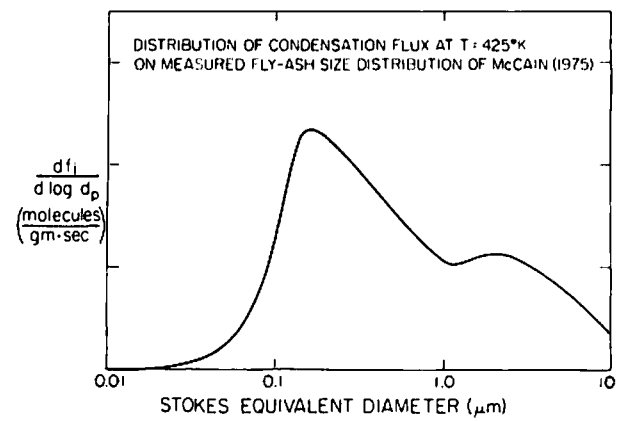

Fig. 9. Calculated distribution of condensation flux to the size distribution measured by McCain et al. [1].

condensation took place earlier in the evolution of the aerosol, the enrichment of submicron particles would be increased because of the larger surface area per unit mass of the smaller particles.

A volatile species that condenses by homogeneous nucleation would probably be uniformly distributed over submicron sized particles since the fine particles undergo considerable growth by coagulation. These fine particles diffuse to the surfaces of larger particles, that is, $F_i \alpha d_p$. Thus we again find that the concentration of the condensing species on particles in the continuum regime would be proportional to d_p^{-2}.

8. SULFATE FORMATION

The particulate matter produced during coal combustion contains high concentrations of sulfur [11]. As has been observed with other volatile species, the sulfur concentration is greater in fine particles than in larger particles. This may be due to the condensation of sulfur trioxide and water to form a sulfuric acid mist. Although only a small fraction of the sulfur in coal is oxidized to form SO_3, the sulfur trioxide has a major impact on boiler operation and aerosol characteristics. Most boiler corrosion appears to be related to the formation of sulfates from SO_3 [37]. The sulfate concentration of fly ash has a strong effect on its electrical resistivity and thus on the collection efficiency of electrical precipitators. The fly ash produced by combustion of low sulfur coals is difficult to remove because of its high electrical resistivity. At some power plants that burn low sulfur coal, SO_3 is added to the flue gases to improve precipitator efficiency.

Cullis and Mulcahy [38] have provided a comprehensive review of the literature on sulfur chemistry and the formation of SO_3 and sulfates in combustion systems, so we only briefly discuss some of the important points influencing the formation of sulfate aerosols within a coal fired boiler. Sulfur contained in fossil fuels is rapidly oxidized to form SO_2 in the high temperature combustion region. Generally less than a few percent of the SO_2 is oxidized to form SO_3 even in the presence of excess oxygen. The thermodynamic equilibrium

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{28}$$

favors SO_3 formation at ambient temperatures. In the presence of the stoichiometric proportion of oxygen at atmospheric pressure, the equilibrium fractions of the sulfur present as SO_3 rather than SO_2 at 575, 775, and 1275°K are about 1, 0.5, and 0.0, respectively. Increasing the oxygen concentration two orders of magnitude changes these figures to about 1, 0.95, and 0.02.

The primary reaction leading to SO_3 production appears to be

$$SO_2 + O + M \rightleftharpoons SO_3 + M \qquad \Delta h_R = -83 \text{ kcal mole}^{-1} \tag{29}$$

Since the concentration of oxygen atoms is much higher than its equilibrium value within the flame front, SO_3 is formed in much greater than equilibrium concentrations in the flame front [38]. This super-equilibrium SO_3 concentration decreases toward the equilibrium value as the combustion products cool.

The equilibrium SO_3 concentration increases with decreasing temperature, but the low equilibrium oxygen atom concentration prevents the formation of SO_3 via the reaction in Eq. 29 at temperatures lower than about 1375°K. Thus the homogeneous gas phase formation of SO_3 occurs primarily in the furnace when temperatures are higher than this value (Fig. 2). Catalysis by heat transfer surfaces of particles may facilitate SO_3 formation at lower temperatures in the convective passes of the boiler.

The total SO_3 formed by homogeneous chemistry in a flame generally accounts for about 1% of the sulfur. Under normal combustion conditions, 10–30% excess air, the conversion of SO_2 to SO_3 is insensitive to the amount of oxygen present in the combustion products as is shown in Fig. 10 [69]. The SO_3 concentration decreases rapidly, however, as the quantity of excess air is reduced.

Catalytic oxidation of SO_2 may occur on the surfaces of fly ash particles in boilers. Ferric oxide and vanadium pentoxide are both efficient catalysts for SO_3 formation. Other species present in the fly ash may reduce the effectiveness of these materials as catalysts. The relative importance of homogeneous chemistry and catalysis to the formation of SO_3 has been a source of controversy. The strong dependence of the SO_3 concentration on the oxygen concentration in the range 0–3% O_2 and the much weaker dependence at high oxygen concentrations is the strongest evidence that most of the SO_3 is formed in the flame. A catalytic mechanism would be expected to produce more SO_3 with increasing oxygen concentration beyond the 3% level. Moreover, the levels of SO_3 produced in coal fired boilers are comparable to those produced in the absence of catalysts.

Sulfur dioxide may also react with ash constituents and metal surfaces. Sodium accounts for about 0.02–0.15% of the coal mass; potassium is about 0.08–0.3% of the coal [47]. These two species readily form sulfates, which are the source of many of the corrosion problems in coal fired boilers. Sodium salts are completely converted to atomic sodium in the high temperature regions of a flame. Sodium intermediates may react with SO_2 or SO_3 to form Na_2SO_4 in the flame, or it may be formed on surfaces. Sodium sulfite is formed under reducing conditions. The chemistry of

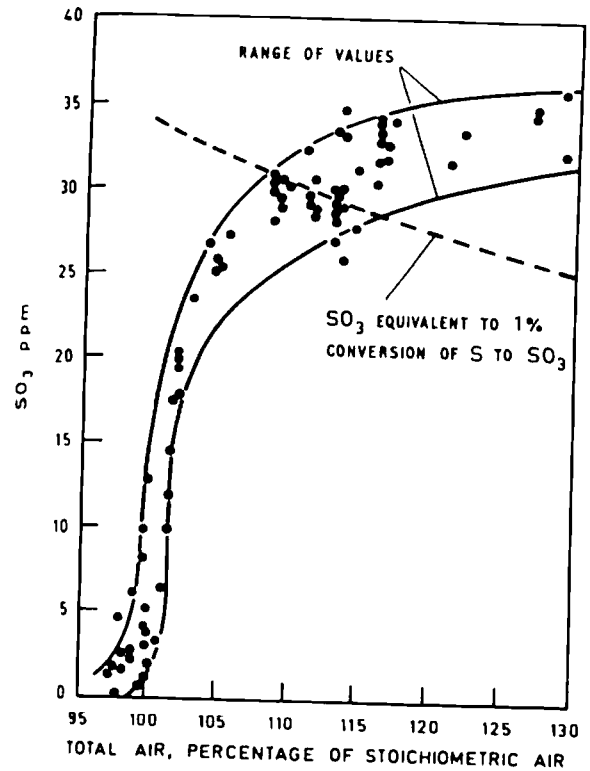

Fig. 10. Effect of excess air on the formation of SO_3 in premixed combustion of natural gas with 5.5 weight percent S as H_2S. (After Ref. 68.)

formation of alkali sulfates and sulfites in flames is poorly understood. Sulfur oxides may also react with other metal oxides, such as Fe_3O_4 [70], to form sulfates.

Sulfur trioxide in the flue gases increases the dew point to as high as 430°K. When the combustion products are cooled below this temperature, SO_3 may condense with water to form sulfuric acid droplets. This condensation may account for a significant fraction of the fine particle mass and cause severe corrosion when it occurs in the boiler or stack. Stack temperatures are usually maintained at higher levels than the dew point to prevent condensation within the plant.

9. CONCLUDING COMMENT

This chapter has reviewed the current understanding of the processes involved in particle formation during the combustion of pulverized coal. Ash derived from the mineral matter in coal accounts for the major portion of the particulate matter produced. It is also the source of many potentially toxic constituents of the particulate emissions. A number of processes that contribute to fly ash formation are summarized in Fig. 11. We have seen that the particle size distribution of ash particles larger than about 1 μm diameter can be related to the coal particle size distribution. This model was based on observations of ash particle formation under conditions similar to those occurring in conventional pulverized coal combustion. New combustion systems may have much different emission characteristics. If coal is burned at temperatures below the ash fusion temperature, the mineral inclusions in a burning coal particle may not agglomerate. The size of the ash particles produced in such a system (e.g., a fluidized bed combustor) may more closely resemble the size distribution of the mineral grains than the coal size distribution. Very high temperature combustion, such as in magnetohydrodynamic power generation, would certainly increase the quantity of ash vaporized.

The formation of submicron sized particles probably occurs by homogeneous nucleation of volatilized ash, soot, and sulfates as well as by the breakup of burning coal particles. The relative contributions of these components can only be determined by further experimental work. Chemical analysis of the submicron aerosol can provide valuable information on the sources of fine particles.

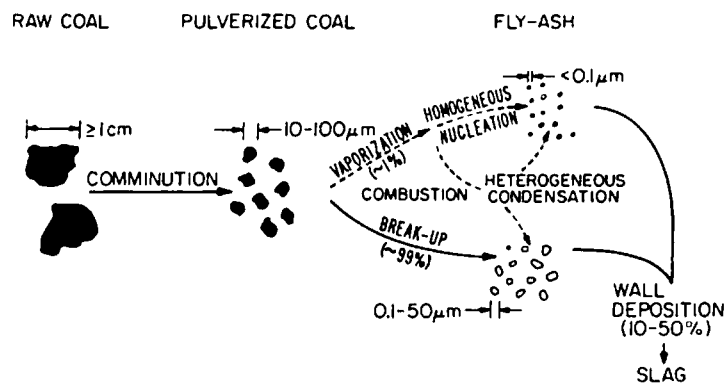

Fig. 11. Processes that contribute to fly ash particle formation.

Simple calculations have shown that condensation can result in substantial enrichment of submicron particles with volatile species. The fraction of a vapor that condenses on fine particles is a strong function of the particle size distribution. The calculations were for heterogeneous condensation on the aerosol present at the inlet to the electrostatic precipitator on a coal fired power plant. This aerosol may contain sulfuric acid and water, which condense at low temperatures. If these components contribute significantly to the submicron aerosol, the surface area of submicron particles available for condensation at higher temperatures is smaller than was assumed in our calculations. The quantity of an ash component that condenses on submicron particles may therefore be less than our calculations suggest. The quantities of sulfuric acid and water contained in the fine particles is not known. Measurements of the composition–size distribution of the fine particles present upstream of gas cleaning equipment will be required to determine the degree to which fine particles are enriched with volatile species.

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REFERENCES

1. J. D. McCain, J. P. Gooch, and W. B. Smith, *J. Air Poll. Control Assoc.*, **25**, 117–121 (1975).
2. O. I. Joensuu, *Science*, **172**, 1027–1028 (1971).
3. K. K. Bertine and E. D. Goldberg, *Science*, **173**, 233–235 (1971).
4. C. E. Billings and W. R. Matson, *Science*, **174**, 1232–1233 (1972).
5. D. H. Klein and P. Russell, *Environ. Sci. Technol.*, **7**, 357–358 (1973).
6. A. W. Andren, D. H. Klein, and Y. Talmi, *Environ. Sci. Technol.*, **9**, 856–858 (1975).
7. C. Block and R. Dams, *Environ. Sci. Technol.*, **9**, 146–150 (1975).
8. C. Block and R. Dams, *Water, Air, Soil Pollut.*, **5**, 207–211 (1975).
9. D. F. Gatz, *Atmos. Environ.*, **9**, 1–16 (1975).
10. G. E. Gordon, D. D. Davis, G. W. Israel, H. E. Landsberg, T. C. O'Haree, S. W. Staley, and W. H. Zoller, "Atmospheric Impact of Major Sources and Consumers of Energy," Progree Report-75, 1 October 1974 to 31 August 1975, University of Maryland, College Park.
11. R. L. Davison, D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr., *Environ. Sci. Technol.*, **8**, 1107–1113 (1974).

12. R. E. Lee, Jr., and D. J. von Lehmden, *J. Air Pollut. Control Assoc.*, **23**, 853–857 (1973).
13. R. E. Lee, Jr., H. L. Crist, A. E. Riley, and K. E. MacLeod, *Environ. Sci. Technol.*, **9**, 643–647 (1975).
14. J. W. Kaakinen, R. M. Jorden, M. H. Lawasani, and R. E. West, *Environ. Sci. Technol.*, **9**, 862–869 (1975).
15. D. H. Klein, A. W. Andren, J. A. Carter, J. F. Emergy, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. Van Hook, and M. Bolton, *Environ. Sci. Technol.*, **9**, 973–979 (1975).
16. R. C. Ragaini and J. M. Ondow, "Trace Contaminants from Coal-Fired Power Plants," presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, September 1975.
17. C. Block and R. Davis, *Environ. Sci. Technol.*, **10**, 1011–1017 (1976).
18. L. J. Shannon, P. G. Gorman, and M. Reichel, "Particulate Pollutant Emission Study: Vol. II. Fine Particle Emissions," EPA Report No. APTD 0744, August 1971.
19. E. J. Schulz, R. B. Engdahl, and T. T. Frankenberg, *Atmos. Environ.*, **9**, 111–119 (1975).
20. E. W. Schmidt, J. A. Gieseke, and J. M. Allen, "Size Distribution of Fine Particulate Emissions from a Coal-Fired Power Plant," *Atmos. Environ.*, **10**, 1065–1069 (1976).
21. *Steam, Its Generation and Use*, Babcock and Wilcox, New York, 1972.
22. J. Lahaye, G. Prado, and J. B. Donnet, *Carbon*, **12**, 27–35 (1974).
23. G. P. Prado, M. L. Lee, R. A. Hites, P. P. Hoalt, and J. B. Howard, "Soot and Hydrocarbon Formation in a Turbulent Diffusion Flame," 649–661, The Combustion Institute, 1976.
24. J. D. Watt and D. J. Thorne, *J. Appl. Chem.*, **15**, 585–594 (1965).
25. E. Raask, *J. Eng. Power*, **88**, 40–44 (1966).
26. E. Raask, *J. Institute Fuel*, **41**, 339–344 (1968).
27. A. R. Ramsden, *J. Institute Fuel*, **41**, 451–454 (1968).
28. A. R. Ramsden, *Fuel* (Lond.), **48**, 121–237 (1969).
29. E. Raask, *Fuel* (Lond.), **48**, 366–374 (1969).
30. I. Fells and D. Richardson, *J. Institute Fuel*, **42**, 245–248 (1969).
31. C. A. J. Paulson and A. R. Ramsden, *Atmos. Environ.*, **4**, 175–185 (1970).
32. J. Yerushalani, M. Kolodney, R. A. Graff, and A. M. Squares, *Science*, **187**, 646–648 (1975).
33. A. S. Padia, "The Behavior of Ash in Pulverized Coal under Simulated Combustion Conditions," D.Sc. thesis, Massachusetts Institute of Technology, Cambridge, Mass., January 1976.
34. G. L. Fisher, D. P. Y. Chang, and M. Brummer, *Science*, **192**, 553–555 (1976).
35. P. Murphy, Jr., J. D. Piper, and C. R. Schmansky, *Trans. ASME*, **73**, 821–843 (1957).

36. E. Raask and D. M. Wilkins, *J. Institute Fuel*, **38**, 255–261 (1965).
37. W. T. Reid, *External Corrosion and Deposits: Boilers and Gas Turbines*, American Elsevier, New York, 1971.
38. C. F. Cullis and M. F. R. Mulcahy, *Combust. Flame*, **18**, 225–292 (1972).
39. B. P. Breen, "Combustion in Large Boilers: Design and Operating Effects on Efficiency and Emissions," presented at the Sixteenth Symposium (International) on Combustion, Cambridge, Mass., August 1976.
40. M. A. Field, D. W. Gill, B. B. Morgan, and P. G. W. Hanksley, *Combustion of Pulverized Coal*, British Coal Utilization Research Association, Leatherhead, England, 1967.
41. R. F. Littlejohn, *J. Institute Fuel*, **38**, 59–67 (1965).
42. R. C. Flagan and J. P. Appleton, *Combust. Flame*, **23**, 249–267 (1974).
43. D. Pratt, *Prog. Energy Combust. Sci.*, **1**, 73–86 (1976).
44. L. Lamb, *J. Institute Fuel* (Lond.), **45**, 443–448 (1972).
45. S. T. Cuffe and R. W. Gerstle, "Emissions from Coal-Fired Power Plants, A Comprehensive Summary," U.S. Public Health Service Report No. AP-35, 1967.
46. J. V. O'Gorman and P. L. Walker, Jr., *Fuel* (Lond.), **51**, 135–151 (1971).
47. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA Report No. EPA-650/2-74-054, July 1974.
48. R. J. Mitchell and H. J. Gluskoter, *Fuel* (Lond.), **55**, 90–96 (1976).
49. C. A. Zappfe, *J.Am. Ceram. Soc.*, **27**, 293–298 (1944).
50. L. Brewer, *Chem. Rev.*, **52**, 1–75 (1953).
51. H. L. Schick, *Chem. Rev.*, **60**, 331–362 (1960).
52. R. J. Ackerman and R. J. Thorn, *Prog. Ceram. Sci.*, **1**, 39–88 (1961).
53. H. Beecher and R. E. Rosenweig, *Amer. Rocket Soc. J.*, **31**, 532–539 (1961).
54. M. Ladadacki, *AIAA J.* **4**, 1445–1447 (1966).
55. F. S. Sinnat, *J. Soc. Chem. Ind.*, Lond. **47**, 151–155 (1928).
56. P. J. Street, R. P. Weight, and P. Lightman, *Fuel* (Lond.) **48**, 343–365 (1969).
57. M. A. Field, *Combust. Flame*, **13**, 237–252 (1969).
58. M. D. Gray, G. M. Kimber, and D. E. Granger, *Fuel* (Lond.) **46**, 399–400 (1967).
59. A. R. Ramsden and I. W. Smith, *Fuel* (Lond.) **47**, 253–256 (1968).
60. F. S. Lai, S. K. Friedlander, J. Pich, and G. M. Hidy, *J. Colloid Interface Sci.*, **39**, 395–405 (1972).
61. S. C. Graham and J. B. Homer, *Faraday Symp. Chem. Soc.*, **7**, 85–96 (1973).
62. S. K. Friedlander, *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior*, Wiley-Interscience, New York, 1977.
63. N. A. Fuchs and A. G. Sutugin, in *Topics in Current Aerosol Research*, G. M. Hidy and J. R. Brock, Eds., Pergamon, New York, 1971.

64. J. Gregory, *Adv. Colloid Interface Sci.*, **2**, 396–417 (1969).
65. J. Visser, *Adv. Colloid Interface Sci.*, **3**, 331–363 (1972).
66. S. Corrsin, *Phys. Fluids*, **1**, 42–47 (1958).
67. C. Park and J. P. Appleton, *Combust. Flame*, **20**, 369–379 (1973).
68. R. W. Linton, A. Loh, D. F. S. Natusch, C. A. Evans, Jr., and P. Williams, *Science*, **191**, 852–854 (1976).
69. R. E. Barrett, J. D. Hummell, and W. T. Reid, *Trans ASME, J. Eng. Power*, **88**, 165–172 (1966).
70. H. H. Krause, A. Levy, and W. T. Reid, *Trans. ASME, J. Eng. Power*, **91**, 216–222 (1969).

EX 1B

Coal Combustion Aerosol Formation Mechanisms: A Review

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The composition and size distribution of particles emitted by coal combustion sources depend upon various mechanisms leading to their formation. A review of current ideas about possible mechanisms for formation of combustion aerosols is presented. Available data regarding fly ash size distribution and elemental concentrations in various size fractions were analyzed. These data were qualitatively compared with theoretical model predictions to indicate the relative contributions of various mechanisms in the formation of aerosols.

INTRODUCTION

With the anticipated increase in use of coal for electric power generation, there is continued concern about the atmospheric emissions associated with coal. Coal combustion is a major source of particulate emissions into the atmosphere. Emission of fine particles in size range 0.1–5 μm in diameter have relatively long atmospheric residence times and may affect health and visibility. These particles are the most difficult to collect by conventional collection equipment (Burchard, 1974; Shannon, 1974).

There is evidence of enrichment or preferential concentration of certain toxic trace elements (e.g., As, Se, Sb, Zn) in the finer fractions of combustion aerosols (Davison et al., 1974; Kaakinen et al., 1975; Ondov et al., 1979a, b; Smith et al., 1979a, b). This raises the question of the respirable emissions from coal combustion as a potential health hazard. The concentration of these trace species increases with decreasing particle size. Thus, it is important to characterize these emissions to assess adequately their health hazards and to facilitate their control.

Combustion aerosols may be characterized by their size as well as their elemental composition. Their characteristics depend on a number of factors, such as the type and properties of the parent coal and the size distribution of the parent coal particles being burned. The composition–size distributions of particles emitted by coal combustion sources are also influenced by furnace design and operating conditions such as temperature. The combustion aerosols contain primarily inorganic matter associated with coal but may also contain unburnt carbon particles—soot, condensed aromatic hydrocarbons, and sulfuric acid droplets. The size and composition of these aerosols depend upon the mechanisms leading to their formation.

Limited data are available regarding detailed size distribution and chemical composition of coal combustion emissions. Careful analysis of these data is necessary to understand the underlying mechanisms involved in their formation. An extensive review of particle formation in coal combustion was made by Flagan and Friedlander (1978). It is the purpose of this paper to analyze and qualitatively compare the data published since this review.

A brief account of coal properties and overall combustion processes is presented first, followed

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by a survey of proposed particle formation mechanisms. Available data are considered first from a particle size distribution point of view. Elemental size distributions are reviewed next. Qualitative comparison of the data is then made with the predictions from various mechanisms.

PROPERTIES OF COAL

Coal structure and composition have definite influence on resulting emissions. The properties vary greatly with coal origin. Even two samples of coal from the same mine may be significantly different.

Distribution and Variability

Coal is distributed widely throughout the United States in the Appalachian, Illinois, and Western basins. Its chemical and physical properties vary greatly from one region to another, as shown in Table 1. The Eastern coals (Appalachian and Illinois) are generally higher in sulfur and iron, producing a more acidic ash than Western coal. Western coal is generally rich in the lighter elements and low in sulfur with a more alkaline ash. Since an extensive study of coal composition has been compiled by Gluskoter et al. (1977), only a limited review will be presented here.

Coal can also be classified by age, as shown in Table 2. Generally, most of the coal consumed for power generation is either bituminous or subbituminous.

Coal Structure

Coal is a complex, heterogeneous, and variable material. Incorporated within the fossilized carbonaceous material are minerals from the original plant tissue and silt deposited during the formation of the coal. In addition, when the coal seam is mined, overburden may be mixed with the coal. Finkelman (1970), in a microscopic analysis of coal, reported that the minerals are dispersed in the coal with diameters ranging down to the submicron region. Sarofim et al. (1977) reported that the inorganic minerals are widely distributed in size with a mean diameter of 1 μm. In addition, clays composed of sub-

TABLE 1. Selected Coal Analysis for the Major Basins in the United States

	Western (28 samples)		Illinois (144 samples)		Appalachian (23 samples)	
	Arithmetic mean	Min:max	Arithmetic mean	Min:max	Arithmetic mean	Min:max
aluminum (%)	1.0	0.3 : 2.2	1.2	0.42: 3.0	1.7	1.1 : 3.1
calcium (%)	1.7	0.44: 3.8	0.67	0.01: 2.7	0.47	0.09: 2.6
chlorine (%)	0.03	0.01: 0.13	0.14	0.01: 0.54	0.17	0.01: 0.80
iron (%)	0.53	0.03: 1.2	2.0	0.45: 4.1	1.5	0.50: 2.6
potassium (%)	0.05	0.01: 0.32	0.17	0.04: 0.56	0.25	0.06: 0.06
magnesium (%)	0.14	0.03: 0.39	0.05	0.01: 0.17	0.06	0.02: 0.15
sodium (%)	0.14	0.01: 1.60	0.05	— : 0.2	0.04	0.01: 0.08
silicon (%)	1.7	0.38: 4.7	2.4	0.58: 4.7	2.8	1.0 : 6.3
titanium (%)	0.05	0.02: 0.13	0.06	0.02: 0.15	0.09	0.05: 0.15
moisture (%)	18	4.1 :13.7	9.4	0.5 :18	2.7	1.0 : 6.8
volatiles (%)	44	33 :53	40	27 :46	33	17 :42
fixed carbon (%)	46	35 :55	49	41 :61	55	45 :72
ash (%)	9.6	4.1 :20	11	4.6 :20	12	6.1 :25
sulfur (%)	0.76	0.34: 1.9	3.6	0.56: 6.4	2.3	0.55: 5.0
heat value (Btu/lb)	11,409	10,084:12,901	12,712	11,562:14,362	13,111	11,374:13,816

From Gluskoter et al. (1977).

TABLE 2. Composition as a Function of Coal Type

Component	Anthracite	Bituminous	Subbituminous	Lignite
moisture (%)	1.4	4.8	18.4	41.5
vol. matter (%)	6.5	32.3	33.8	23.0
fixed carbon (%)	79.5	51.2	39.0	20.9
ash (%)	12.5	11.7	8.8	14.6
hydrogen (%)	2.4	5.0	5.9	6.8
carbon (%)	80.1	69.1	54.3	29.9
nitrogen (%)	0.8	1.3	1.0	0.5
oxygen (%)	3.2	10.3	29.3	46.5
sulfur (%)	0.8	2.7	0.7	1.7
heat value (Btu/lb)	12,780	12,260	9140	5000
sulfate sulfur (%)	0.02	0.16	0.04	0.24
pyritic sulfur (%)	0.35	1.70	0.35	0.68
organic sulfur (%)	0.48	0.88	0.32	0.75

From Swanson et al. (1976).

micron particles may be incorporated in the coal. It appears from the rather limited studies on coal that the mineral inclusions are submicron and vary over a wide range of sizes. However, very few quantitative data on coal-mineral size distribution exist. Major forms of the minerals appear to be aluminosilicates with pyrites, calcites, and magnesites in various proportions (Gluskoter et al., 1981).

COMBUSTION PROCESS

Qualitative Description

Pulverized firing systems are most commonly used for large modern power plants using coal (Babcock and Wilcox, 1978). The crushed coal from the mine is pulverized into a fine powder, usually 100–200 mesh. The mean mass diameter of coal particles may vary from plant to plant, and the size distribution is usually very broad. The pulverized coal is blown into the furnace with carrier air. Coal particles are heated by radiation and mixing with hot gases. Combustion temperature depends upon percent excess air, quality of coal, and effectiveness of mixing. Temperatures up to 2000°C are usual. Different coal particles may be subjected to varying temperatures due to differences in size and nonuniformity in mixing.

A number of processes may occur during coal-particle burnout. As a coal particle is being heated, it may mechanically break up into fragments because of thermal stresses induced by internal fissures, cracks, and structural imperfections initially present (Flagan and Friedlander, 1978). Volatile fractions originally present in the coal or formed by pyrolysis are vaporized. Chemical decomposition may take place evolving gaseous CO_2, SO_2, and SO_3. A particle may burst open from pressure generated internally by evolution of such gases (Smith et al., 1979b). A heated coal particle swells and may become porous. The degree of swelling depends both on the coal type and combustion conditions.

The general range of behavior of solid particles during gas–solid reactions was discussed by Levenspiel (1962). In extreme cases a coal particle may either retain the ash layer as burning proceeds inward or continuously shed the ash layer as the particle burns and thus shrink in size (Figure 1). The physical state of the ash layer would depend upon ash temperature and mineral composition. The shedding of ash layer may be caused by the evolution of off gases or by cracking or breakup of the particle.

Three temperature ranges that have varying influence on the behavior of mineral inclusions may be indicated. At low enough temperatures the mineral ash inclusions may remain solid. These inclusions may undergo chemical trans-

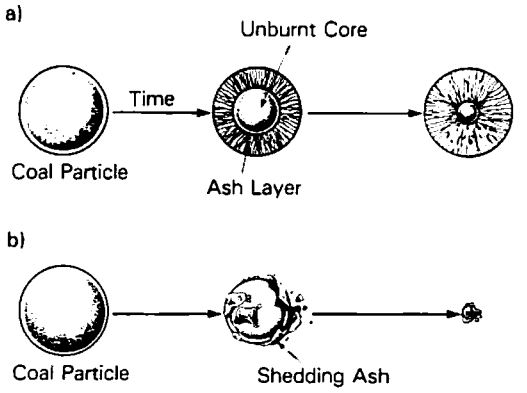


FIGURE 1. Two extreme types of coal particle combustion: coal particle burning (a) at constant size and (b) with shrinking size.

formations such as decomposition as well as physical transformations such as sintering. A medium temperature range may be designated as the one at which mineral inclusions may fuse, thereby producing highly viscous molten ash. At higher temperatures the viscosity of molten ash is considerably reduced with increased fluidity. The actual temperature values for these ranges would depend upon the mineral ash compositions involved.

The individual mineral inclusions, whether solid or liquid, eventually form the resulting fly ash particles. These inclusions may undergo several physical transformations modifying their size distribution.

Coalescence of Individual Mineral Inclusions. Molten mineral ash inclusions present on a burning coal particle may coalesce and form larger ash droplets. For low combustion temperatures, where the ash remains solid, obviously there would be no coalescences, although some sintering may take place joining adjacent solid small particles. The higher the temperature, the greater the extent of coalescence that may be expected, because of the higher mobility of molten ash. The extent of coalescence may be expected to be greatly reduced with significant shedding of ash. Uncoalesced mineral inclusions and shedded ash may eventually form fine particles.

Bubble Formation. Molten mineral inclusions may come together to form a liquid layer. Gases may evolve within this layer so as to form bubbles. At medium temperatures, because of high viscosity these bubbles may remain stable and form large hollow spheres or cenospheres (Sarofim et al., 1977). At high temperatures, however, these bubbles may burst open owing to lower ash viscosity releasing fine molten ash droplets (Smith et al., 1979b). Bubble-bursting phenomena are not yet well understood, and any conclusive evidence in support of this mechanism has not yet been provided. Based upon aqueous bubble-bursting studies reported in the literature (Tomaides and Whitby, 1975), a broad bimodal droplet size distribution may be expected from such ash bubble bursting. Again in this case, shedding of ash may be expected to reduce the extent of bubble formation.

Evaporation and Condensation of Relatively Volatile Species. An ash species may vaporize depending upon the ash temperature, composition, and relative volatility of the species concerned. The volatility of an element depends on its chemical form in the ash. Thus observed elemental volatilities may be expected to be different from pure element-relative volatilities. Because of the reactive atmosphere near a particle surface, several chemical reactions are possible modifying the volatility of a species. A reducing or oxidizing atmosphere may prevail in the vicinity of a coal particle, depending on the mixing of gases, percent excess air, kinetics of combustion reactions, and presence of an ash layer surrounding the "burning front" that may introduce diffusional effects. Close to a particle surface reducing conditions may be expected whereas slightly away from the coal particle oxidizing conditions may be present in the gas phase. This model was proposed by Levenspiel (1962) to explain solid gas reaction kinetics and is diagramed in Figure 2. The reducing conditions near the particle surface may produce more volatile, reduced species that would vaporize, oxidize in the bulk gas phase away from the particle surface, and subsequently condense owing to the lower volatilities of oxidized species, e.g., SiO (Sarofim et al., 1977).

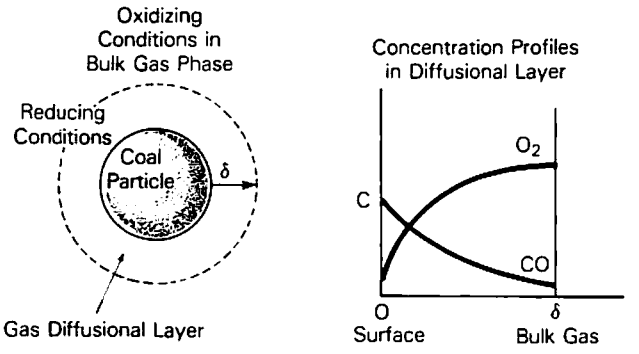


FIGURE 2. Reducing boundary layer at the particle surface.

The vaporized species may condense downstream upon gas cooling, either homogeneously forming new very fine, rapidly coagulating particles or heterogeneously condensing on existing particles. The fine particles and particle surfaces in general would then be preferentially enriched with volatile species. The degree of enrichment would depend upon the volatility of the species in question.

Homogeneous condensation would result in bulk enrichment of volatilized species in the fine size fractions. Heterogeneous condensation, on the other hand, would result in surface enrichment of the volatilized species. The enrichment would be most prominent in the finer size fractions because of their greater available surface area for condensation per unit volume.

In addition to these three major processes, several other mechanisms are also possible. Some fine mineral inclusions may remain separate without coalescing with others owing to surface tension effects or simply adequate spatial separation from other molten inclusions. These fine inclusions may eventually detach to form fine particles. Extraneous clay particles that adhere to the coal during mining and processing may easily disintegrate, separate out, and pass through the combustion process unchanged. Some fraction of carbon may remain unburnt and appear in the aerosols. Aromatic hydrocarbons may vaporize and burn and partially release fine carbon particles, or soot (Green and Lane, 1964).

The minerals may form solid solutions and may exhibit different properties as compared to individual species in the solution. This apparently affects relative volatilities of some species. Thus, elements structurally incorporated into aluminosilicate matrix tend to show reduced volatility, e.g., Na. A physical rearrangement within the solid solutions similar to dissolution and precipitation may also be possible in varying temperature conditions.

Figure 3 presents a qualitative picture of what might be happening during the combustion and shows the multitude of processes that may be occurring simultaneously.

Particle Formation Mechanisms

Although a number of mechanisms of qualitative nature have been proposed, a semiempirical quantitative treatment has been developed for two mechanisms.

Breakup Model. A detailed account of this model is presented by Flagan and Friedlander (1978). The model considers melting of mineral inclusions followed by coalescence as the combustion front recedes. Each coal particle is then assumed to yield a number P of particles of equal size. Knowing the coal particle size distribution, the mass fraction of mineral ash, and the densities of coal and ash fractions, an ash particle size distribution may be predicted for a given value of P.

The mean mass diameter of ash may be given as adapted from Flagan and Friedlander (1978).

$$\bar{D}_{ash} = \sqrt[3]{\frac{f}{P}\frac{\rho_c}{\rho_a}}\,\bar{D}_{coal} \qquad (1)$$

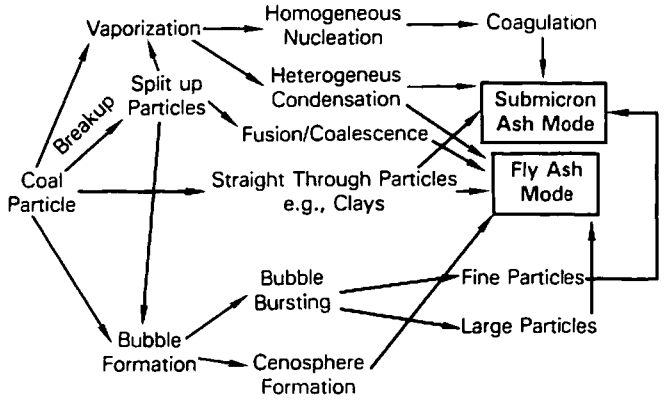


FIGURE 3. Schematic of coal combustion aerosol formation.

where

$\bar{D}_{coal}$ is the mass mean diameter of coal (μm),

$\bar{D}_{ash}$ the mass mean diameter of ash (μm),

ρ_c the density of coal (g/cm^3),

ρ_a the density of ash (g/cm^3),

P the number of coal fragments produced per particle, and

f the mass fraction of ash in coal.

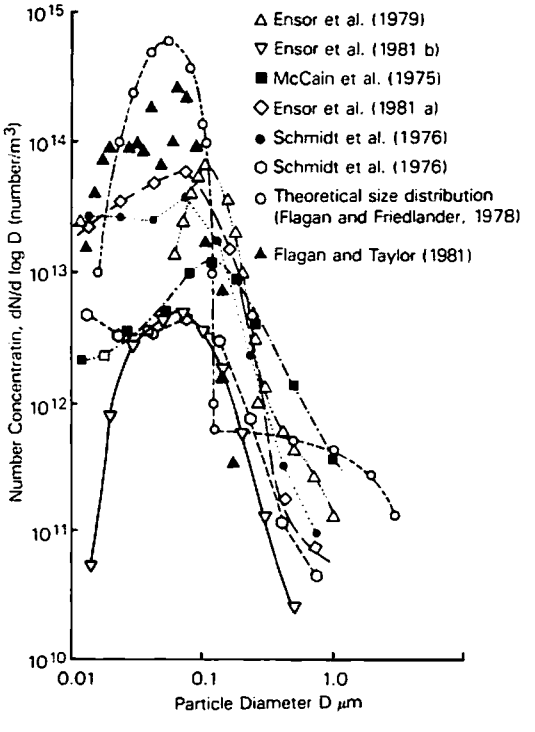
Equation (1) is a simplified view of the ash formation process. The value of P is usually considered to be between 3 and 5. Laboratory studies by Sarofim et al. (1977) are consistent with this model.

Since Eq. (1) implies that the ash forming process from each coal particle is similar in the breakup model, all resulting ash particles are predicted to be similar in their physical, morphological, and chemical nature. No explanation of cenospheres or fine submicron particles is contained in this model.

Vaporization–Condensation Model. This model suggests a mechanism for submicron particle formation. Basically a fraction of ash ($\sim 1\%$) is assumed to be vaporized and homogeneously condensed to form primary particles of the order of 10 Å in size, followed by coagulation to yield self-preserving particle-size distribution within a few seconds (Flagan and Friedlander, 1978). Such a process predicts a submicron mode in particle size distribution around 0.1 μm.

The resulting size distribution, when compared with the fine particle data of McCain et al. (1975), was found to predict an order of magnitude larger number of particles with a smaller mean diameter (Figure 4). Flagan (1979) later included accelerated coagulation due to interparticle dispersion and nonhomogeneous

FIGURE 4. Aerosol size distribution in the submicron range.



mixing, which reduced the discrepancy but still predicted larger than observed fine particle densities. Additional recent data (Ensor et al., 1979, 1981a) also showed similar discrepancies between theory and experimental observations.

The model has some flexibility through the empirical parameter—the fraction of ash vaporized. This fraction would actually depend upon ash mineral composition and temperature. The model predicts a sharp submicron mode in mass or number size distribution at about 0.1 μm. Vaporization of species depends upon their relative volatilities. Hence, such a submicron ash mode formed by vaporized material may be expected to be composed primarily of volatile materials, and its composition may be expected to differ significantly from larger particles formed in breakup. This model has also been strongly supported by laboratory combustion studies (Sarofim et al., 1977; Mims et al., 1979; Flagan and Taylor, 1980; Neville et al., 1980).

Other mechanisms that have not been quantified but have been justified by experimental observations are as follows:

1. Bubble formation due to evolution of gases in the coal particles. This mechanism has been supported by the presence of large cenospheres observed microscopically by various investigators. Laboratory studies by Sarofim et al. (1977) indicated the mass fraction of cenospheres to be dependent upon temperature and to peak at 6% at 1500 K.
2. Condensation of volatile species on existing particles to produce surface layers enriched in volatile species. Numerous observations have indicated surface enrichments of volatile species, especially on fine particles. The concentration of certain volatile species has been observed to increase with decreasing particle size. Biermann and Ondov (1980) have recently analyzed their surface enrichment data to indicate a $C \propto 1/d^2$ relationship.
3. Bubble bursting at high temperatures as a source of fine particles with compositions similar to the large-particle parents (Ramsden, 1969; Smith et al., 1979b). No quantification of particle size distribution resulting from bubble bursting has been made. Conclusive evidence for this mechanism is yet to be provided.

These mechanisms may now be compared with some of the available data regarding mass-size distribution and elemental-size distribution.

PARTICLE SIZE DISTRIBUTION

Measurement Techniques

The measurement of aerosol size distributions should be reviewed before examining the data and comparing them to theories. The study of experimental techniques is still a research activity. Major problems with measurements and data analysis include these:

a. In situ cascade impactors have limited resolution of particle populations greater than 10 μm because of wall and inlet nozzle losses (Cushing et al., 1976; Knapp, 1980). Lower cutpoint is usually limited to about 0.2 μm. Impactors may have problem with particle bounce and reentrainment, which is especially serious for lower range of cut sizes.
b. Extractive sampling to condition stack gas for measurement by electrical aerosol analyzers (EAA) and optical particle counters introduces a bias in the particles larger than 1 μm. Also, a large dilution of stack gas sample is necessary to use these instruments. The EAA data for combustion aerosol should be corrected for cross sensitivities of neighboring channels (Markowski et al., 1980). The sharpness of the submicron mode *may* also be affected by coagulation within the sampling probe.

In general, conventional impactors are best suited for the size range of 0.5–10 μm, whereas EAA has better resolution in the submicron range. Diffusion batteries have also been used (McCain et al., 1975) for submicron ash analysis, but this instrument does not have cutpoints that are as sharp as those of EAA. The smallest cutpoint diameter of an impactor may be lowered further by operating the impactor under subatmospheric pressures. Particles as small as

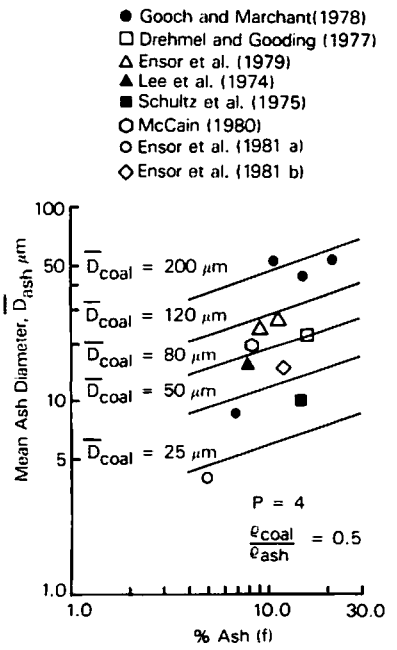
0.02 μm can be impacted under partial vacuum because resistance from air molecules is reduced (Pilat, 1978; Flagan, 1981). This technique was successfully used by Ensor et al. (1981b) for field experimental evaluations and in the laboratory by Flagan and Taylor (1980).

Coarse Ash Fraction

Available data indicate that the majority of fly ash is above 1 μm in size with a broad peak in the range of 3–50 μm diameter. The actual mass mean diameter and shape of the size distribution depend upon several factors, such as coal type and composition and coal-particle size distribution. The large diameter mode may be called a *fly ash mode* and is generally explained by the breakup model, with P being the number of fragments produced per coal particle as a variable parameter. Laboratory data by Sarofim et al. (1977) indicate that P ranges from 3 to 5. With this model the mean ash diameter is given by Eq. (1). In Figure 5 the literature data on coal ash concentration and mean particle diameter are compared to curves predicted with Eq. (1) (Ensor, 1980). The value of P was assumed to be 4 and ρ_c/ρ_a to be ~ 0.5. Since all the data correspond to pulverized coal-fired systems, the mean coal particle diameter is expected to be ~ 80 μm. Only fair agreement with the model is seen. Several reasons are believed to contribute to the differences.

1. The accuracy of impactor measurements in determining ash size distribution may not be sufficient. Usually data are truncated at 10 μm and extrapolated assuming a log-normal distribution. This approximation can lead to large errors in mean ash diameter.
2. The coal size distribution is usually not known accurately at the time of the impactor measurements.
3. Usually some mass fraction of the ash is composed of cenospheres (up to 5%). Since these are large particles with lower density, a bias in the ash size distribution may be introduced.
4. The parameter P is assumed to be constant for all coal particle sizes. However, it may be a function of coal size and type. For a given coal type, the mean ash diameter may be reasonably expected to depend on mean coal particle size.
5. Morphological analysis of a coal flyash sample by Fisher et al. (1978) indicated 11 major classes of fly ash particles. The breakup model, on the other hand, predicts only particles of similar physical and chemical nature.

FIGURE 5. Mean fly ash particle diameter for uncontrolled sources as a function of coal ash mass fraction.



Submicron Ash Fraction

Submicron ash usually makes up less than 2% of the total fly ash mass. The lowest cutpoint diameter of a conventional cascade impactor is about 0.2 μm. With a low pressure impactor the cutpoint diameter can be lowered up to 0.02 μm (Ensor et al., 1981b; Flagan and Taylor, 1980), but the quantity collected on submicron stages is usually too small to weigh accurately. As a result, an impactor has limited sensitivity in the submicron range. Much better sensitivity in the

submicron range is obtained by an EAA or a diffusion battery technique.

A distinct submicron mass mode was observed around 0.1 μm diameter when these instruments were used for analysis. McCain et al. (1975) found a broad submicron peak in number distribution by taking measurements with a diffusion battery. The peak reported by McCain disappears when size distribution is plotted on a mass basis. Sharper submicron peaks were observed when measurements were made by an EAA (Schmidt et al., 1976; Ensor et al., 1979; Flagan and Taylor, 1980; Markowski et al., 1980). These data retained the peaks when plotted on a mass basis. Peaks are especially sharp when the data reduction process takes into account cross sensitivities of neighboring channels of the EAA (Markowski et al., 1980). Ondov et al. (1979b) analyzed the impactor filter samples with scanning electron microscopy (SEM) and detected a mode at 0.16 μm. Particles were sized and counted from SEM photographs for this purpose.

These observations tend to support qualitatively the vaporization–condensation mechanism that predicts a submicron mode at 0.1 μm due to coagulation. When the observed number concentration of submicron particles from field measurements is compared with theoretical predictions, one or two orders of magnitude discrepancies are seen (Figure 4). The agreement is much better for the laboratory data taken by Flagan and Taylor (1980). Part of the discrepancies in field measurements may be explained by coagulation in the sampling probe. The difference in the submicron distribution data by Ensor et al. (1979, 1981a, b) taken with similar equipment and procedures at various sites indicates a strong influence of coal composition on the magnitude of the submicron distribution peak. Site-dependent variability was reported by McElroy et al. (1982).

ELEMENTAL SIZE DISTRIBUTIONS

Measurement Techniques

Several analytical techniques have been developed for the elemental analysis of a sample and have been summarized by Smith (1980). The most commonly used techniques are

1. x-ray fluorescence analysis (XRF),
2. instrumental neutron activation analysis (INAA),
3. atomic absorption analysis (AAA), and
4. x-ray photoelectron spectroscopy (ESCA).

The first three (XRF, INAA, and AAA) analyze bulk or volume samples, whereas ESCA analyzes the surface. A sputter-etching technique is normally used to remove surface layers of different depths and to expose internal material.

Sample preparation for analysis is of course an important step. Size-classified samples are required to determine elemental size distributions and concentrations. Most commonly, samples are collected on cascade impactor stages for later analysis for chemical compositions. In this scheme a filter collects all particles below the cutpoint of the last impaction stage, usually 0.2 μm. With the low pressure impactor it has been possible to collect samples of particles down to 0.02 μm; however, only limited data using this technique are available (Ensor et al., 1981b). Since the low pressure impactor has a larger number of stages, the possibility of contamination due to larger particles bouncing off from preceding stages is minimized. In a conventional impactor, with fewer stages and a lowest cutpoint diameter of 0.2 μm, the larger particles bouncing off from earlier stages are likely to contaminate the submicron fraction collected on the filter.

Impactor sampling provides in situ samples. Some analyses have also been made on bulk fly ash samples collected by control equipments. This ash was later size classified by techniques such as elutriation to provide samples for elemental analysis (Ondov et al., 1978; Desrosiers et al., 1979; Smith et al., 1979b). This scheme has been controversial. This procedure would work well provided there are no physical or chemical changes in accumulation and redispersion of the fly ash samples. This is probably the case for larger particle sizes. For small particles, however, particle interactions are expected to become significant. Upon collection and accumulation, small particles are likely to

agglomerate among themselves to form larger ones; they also may adhere to larger particles. The smaller the particle is, the more energy that is required to separate it. With higher energy abrasion of large particles, the generation of "new" fine particles may become significant. Thus redispersion of collected fly ash, especially of the fine fraction, may introduce some measurement artifacts.

Data Analysis

Elemental size distribution data are only recently being investigated, and the techniques are still in experimental stages. The limited amount of data therefore understandably shows variations (e.g., Klein et al., 1975; Block and Dams, 1976).

Some broad generalizations may be made from the data obtained on coal-fired utility boilers. Most of the mass of ash is composed of so-called aluminosilicate matrix elements. These include Al, Si, Ca, Mg, and Fe. Na, K, and Ti are also usually present in significant quantities. The proportions of each of these elements depends on the coal type used. These elements are generally found in all size fractions, including submicron fractions, in similar proportions.

Most of the data show distinct enrichments of trace elements– As, Se, Sb, Zn, Mo, Pb, Ga, and Cd—in the finer size fractions. Enrichment has also been reported for W, but the data are limited. These may be called group I elements. A second group of elements may be made which show slight depletion or no change in elemental concentration with respect to particle size. These include Al, Si, Fe, Ca, Ti, Mg, K, Ce, Hf, and other rare-earth elements. A third grouping of elements includes those that show slight enrichment or intermediate undeterminable behavior. Also included in this group are those elements for whom conflicting trends have been reported. The group III elements include Ba, Sr, Ni, Cr, Co, Mn, Na, U, and V.

These groupings have been made to indicate general trends. Unusual behaviors have also been reported, e.g., slight enrichment of Ca (Ondov et al., 1979a), slight enrichment of Fe (Smith et al., 1979a), no change with Zn and Ga (Gladney et al., 1976), enrichment of Ti (Ondov et al., 1979b), depletion of Fe and of Ce relative to Al (Gladney et al., 1976), etc. These observations and the conflicting reports for group III elements may be the effect of coal type, different operating parameters (such as combustion temperature), and inaccuracies involved in sampling and analytical procedures.

Strong evidence of surface enrichments attributable to evaporation of volatile species followed by heterogeneous condensation have been found by Linton et al. (1976), Smith et al. (1979a, b), Hansen and Fisher (1980), Neville et al. (1981), and several other investigators. Since small particles have higher surface area-to-volume ratio, the enrichment is expected to increase with decreasing particle size. From simple geometrical considerations, Davison et al. (1974) proposed that the enrichment concentration of volatile species should be proportional to $1/d$, where d is fly ash particle diameter. For the continuum regime, condensation indicates $c \propto 1/d^2$ (Flagan and Friedlander, 1978). Flagan found that both relations fit reasonably well to data by Davison et al. (1974). Biermann and Ondov (1980) found better agreement with the $1/d^2$ relationship when data are taken with a cascade impactor of high resolution in the submicron range. Data taken with a conventional cascade impactor are usually available only to 0.2 μm. Extrapolation of the above relationship to the finer size range may be potentially misleading as it would predict a rapid increase in surface concentrations for every volatile element. Such extrapolations by Biermann and Ondov (1980) show that a particle of pure condensed material would have a diameter of 0.045 μm. The data taken with a low pressure cascade impactor (with a smallest cutpoint diameter of 0.02 μm), on the other hand, indicated an absence of particles below 0.08 μm (Ensor et al., 1981b).

Contrary to findings by Biermann and Ondov (1980) and others, data by Smith et al. (1979a, b) indicate the concentration of most of the volatile species in size fractions smaller than 1 μm to be independent of size. There is definite enrichment of volatiles in these particles com-

pared with their concentration in larger particles. The concentrations have been shown to increase as the particle size decreased from 10 to 1 μm, where it levels off. These data were obtained by separating hopper ash, instead of in situ impactor sampling as used by several other researchers (Ensor et al., 1979, 1981 a, b; Biermann and Ondov, 1980). This discrepancy may be explained as measurement artifacts, as discussed earlier. Smith et al. (1979b) suggest bursting of bubbles as a possible mechanism for the formation of such fine particles.

The effect of matrix structure and surface segregation was pointed out by Stinespring and Stewart (1981). They showed that, at the elevated temperatures experienced during and after the combustion process, diffusive transport of the trace and minor elements to the surface of the ash particles (i.e., surface segregation) could contribute to the observed surface enrichment. Such processes require residence times of several hours at elevated temperatures to be significant in combustion processes. However, such processes may be possible after collection and deposition of fly ash particles or in advanced combustion processes utilizing fluid beds.

A common observation in the majority of the field data is the presence of relatively less volatile major matrix elements in the fine submicron fractions. These are seen even in the nearly monodisperse submicron modes observed by Ensor et al. (1979, 1981b). A submicron mass mode is qualitatively explained by the vaporization condensation mechanism, as discussed earlier. However, the submicron mode may also be expected to be considerably depleted in less volatile species. To explain the presence of less volatile species like Al and Si in submicron fractions, a reduction of the refractory species Al_2O_3, SiO_2, and MgO to more volatile reduced species AlO, SiO, and Mg in the reducing zone near the burning particle surface has been suggested (Sarofim et al., 1977; Desrosiers et al., 1979; Mims et al., 1979; Neville et al., 1980). The vaporized reduced species may later oxidize in the oxidizing gas atmosphere away from the particle. The oxidized species would then condense out, because of their low volatility. To predict resulting submicron ash composition, kinetic data related to the listed reactions and thermodynamic data related to all compounds involved are needed. Such predictions, made by Ulrich et al. (1977) for a cyclone coal-fired boiler ash, were compared with experimental fly ash composition. Considerable discrepancies regarding Al_2O_3, CaO, and FeO compositions were observed and were attributed to the mixing of two sets of fine ash particles, one originating by vaporization-condensation and the other having composition similar to large particles and entrained by some other mechanism (Desrosiers et al., 1979). It may be pointed out that the presence of major matrix elements in submicron ash may also arise simply as an artifact of sampling technique, e.g., larger particles bouncing off impactor stages onto the filter.

Based on the vaporization mechanism, the relative volatilities of the species in the three groups may be expected to be in the following order:

group I > group III > group II.

Such an order, however, does not follow the expectations based on the volatility data of pure species or compounds. (Table 3 gives the boiling points of the elements and their compounds.) For example, Mg and K from group II are relatively more volatile than Ba, Sr, or Mn of group III. Also, it appears that for some species their specific chemical compounds need to be formed to justify their relative high volatility. Thus, for Ni and Mo, their carbonyls appear to be the volatilizing species. Halides seem to be the choice for U, V, Co, Cr, Sb, and Mn. The lower volatilities experienced by Na, K, and Mg may perhaps be explained if they are considered to be structurally incorporated into an aluminosilicate matrix structure.

Laboratory studies under controlled conditions by Sarofim et al. (1977) and by Flagan and Taylor (1980) show much different results compared with field studies regarding the behavior of major matrix elements. The role of evaporation and submicron ash composition were clearly shown to be a function of tempera-

TABLE 3. Boiling Points of Elements and Their Compounds

Species	Boiling point (°C)
As	613 (sublimes)
Se	685
Sb	1750
$SbCl_3$	283
Zn	907
ZnO	>2500
Mo	4612
$Mo(CO)_6$	156
MoO_3	1155 (sublimes)
Cd	765
Pb	1740
Al	2467
Al_2O_3	2980
Ca	1484
CaO	2850
Si	2355
SiO	1880
SiO_2	2230
Ti	3287
$TiCl_4$	136
Mg	1090
MgO	3600
K	774
Ba	1640
BaO	>2000
Sr	1384
SrO	>3000
Ni	2732
NiO	>3000
$Ni(CO)_4$	43
Cr	2672
Cr_2O_3	4000
CO	2870
CoO	>2000
Mn	1962
$MnCl_2$	1190
Na	883
U	3818
UCl_4	792
V	3380
VCl_4	148

From Perry and Chilton (1973).

ture and reflect the effect of reaction kinetics and relative volatilities of the species (Mims et al., 1979; Neville et al., 1980). More volatile Mg, Fe, and Na were considerably enriched, and Al and Ca were correspondingly depleted. Results with Si analysis indicated dependence upon coal type and structure. The nature and chemical composition of mineral species were found to effect its reactivity and volatility. The work of Flagan and Taylor indicated a large percentage of soot (unburned carbon), as well as sulfur in the submicron mode. The high concentration of Si in submicron fractions observed in these laboratory studies may be explained by formation of more volatile SiO near the particle surface because of the presence of reducing conditions. The submicron size distribution observed in Flagan and Taylor's work is in good agreement with that predicted by vaporization–homogeneous condensation mechanism. Thus the laboratory studies tend strongly to support the vaporization–condensation model for submicron particle formation.

CONCLUSIONS

(1) The formation of fly ash particles larger than 1 μm is reasonably explained by coal-particle breakup and the coalescence of molten grains of mineral matter during combustion. Cenospheres caused by inflation of the molten ash depend on the ash viscosity, but in most circumstances it is only a small fraction of the total ash on a weight basis. Laboratory data suggest the parameter P in the breakup model (indicating number of ash particles formed per coal particle) to be between 3 and 5. The data obtained from commercial coal-fired boilers show only moderate agreement with the model. This discrepancy may be primarily due to the difficulty in obtaining accurate particle size distributions above 10 μm in field tests.

(2) The physical particle size distribution in the less than 1 μm range is qualitatively explained by a vaporization–homogeneous condensation mechanism. The most likely explanation of the submicron mode observed in various field and laboratory data is vapor-to-particle conversion. Also, the concentration variability of submicron particles is indicative of a temperature and coal composition dependence. The concentration of submicron particles determined in field measurements on commercial scale boilers is, however, lower, often by two

orders of magnitude, than the laboratory measurements and theoretical predictions. Part of the explanation may be the coagulation of the submicron material in the sampling systems used in field tests. However, some of the field-size distributions (Ensor et al. 1981a) obtained with equipment designed to minimize coagulation did not appear to be significantly different than the other field data.

(3) The elemental size distribution from field measurements on commercial scale boilers indicates that the ash is mostly composed of so-called aluminosilicate major matrix elements. These are generally found in all size fractions, including submicron fractions, in similar proportions. These observations are not consistent with a simple vaporization–homogeneous nucleation model for submicron particle formation. Alternative mechanisms suggested for the formation of such fine particles containing aluminosilicate matrix elements include (a) the presence of extraneous submicron particles not associated with coal such as clays, (b) mineral inclusions released as submicron particles without coalescence (c) the bursting of molten ash bubbles releasing fine submicron particles, and (d) the reduction of matrix elements at the coal particle surface during combustion, producing more volatile species.

The laboratory studies with controlled combustion conditions indicate a greater concentration particle size dependence for major matrix elements than reported from field tests. The laboratory results are consistent with the vaporization homogeneous condensation mechanism, with the enrichment and depletion of a species depending on its relative volatility. The enrichment of silicon in fine-size fractions is considered to be due to formation of volatile SiO in the reducing atmosphere near the coal-particle surface, while aluminum is depleted in the fine-size fractions. The elemental size distributions are also found to depend on coal composition. The laboratory particle separation experiments have been conducted under conditions to minimize measurement artifacts introduced by impactors, which may have been significant in field tests.

(4) The observed particle surface enrichment by trace volatile species over the whole size range is generally explained by a vaporization–heterogeneous condensation mechanism. The enrichment is especially dominant in fine-size fractions owing to their higher surface area to volume ratio compared to coarse size fractions. The concentration of trace species increases with decreasing particle size and is found to vary as $1/(\text{particle diameter})^2$ with reasonable accuracy for limited data.

REFERENCES

Babcock and Wilcox (1978). *Steam/Its Generation and Use*, 39th ed., New York.

Biermann, A. H., and Ondov, J. M. (1980). Applications of surface-deposition models to size-fractionated coal fly ash, *Atmos. Env.* 14:289–295.

Block, C., and Dams, R. (1976). Study of fly ash emission during combustion of coal, *Environ. Sci. Technol.* 10:1011–1017.

Burchard, J. K. (1974). The significance of particulate emissions, *J. Air Poll. Control Assoc.* 24:1140–1142.

Cushing, K. M., Lacey, G. E., McCain, J. D., and Smith, W. B. (1976). Particulate sizing techniques for control device evaluation: Cascade impactor calibration, EPA Rep. 600/2-76-280, October.

Davison, R. L., Natusch, D. F. S., Wallace, J. R., and Evans, C. A., Jr. (1974). Trace elements in fly ash dependence of concentration on particle size, *Eviron. Sci. Technol.* 8:1107–1113

Desrosiers, R. E., Riehl, J. W., Ulrich, G. D., and Chiu, A. S. (1979). Submicron fly ash formation in coal fired boilers, *Proc. 17th symp. Combust., Combust. Inst.*, 1395–1403.

Drehmel, D. C., and Gooding, C. H. (1977). Field tests of a hot-side electrostatic precipitator. Proceedings: particulate collection problems using ESPs in the metallurgical industry, EPA Rep. 600/2-77-208, October.

Ensor, D. S., Cowen, S., Hooper, R., Markowski, G., Scheck, R., Farrell, J. D., and Burnham, J. (1979). Evaluation of the george meal No. 3 electrostatic precipitator, EPRI Rep. FP-1145, August.

Ensor, D. S. (1980). Stationary source aerosol emissions, presented Symp. Plume and Visibility: Measurements and Model Components, Grand Canyon, AZ, November.

Ensor, D. S., Lawless, P. A., Damle, A. S., and Sparks, L. E. (1981a). Evaluation of the United McGill electrostatic precipitator, presented at the EPA 3rd Symp. Transfer and Utilization of Particulate Control Technology, Orlando, FL, March.

Ensor, D. S., Cowen, S., Shendrikar, A., Markowski, G., Wolfinden, G., Pearson, R., and Scheck, R. (1981b).

Kramer station fabric filter evaluation. EPRI Rep. CS-1069, January.

Finkelman, R. B. (1970). Determination of trace element sites in the Waynesburg by SEM analysis of accessory minerals, *Scanning Electron Microscopy* 1:60.

Fisher, L. L., Prentice, B. A., Iberman, D. S., Ondov, J. M., Bierman, A. H., Ragaini, R. C., and McFarland, A. R. (1978). *Environ. Sci. Technol.* 12:447–451.

Flagan, R. C. (1979). Submicron particles from coal combustion, *Proc. 17th Symp. Combustion, Combustion Inst.*, 97–104.

Flagan, R. C. (1981). Temperature and pressure effects in low pressure cascade impactors, presented at ACS-81 Winter Symp. Aerosol Sci. Tucson, AZ, January.

Flagan, R. C., and Friedlander, S. K. (1978). Particle formation in pulverized coal combustion—a review, in *Recent Developments in Aerosol Science* (D. T. Shaw, ed.), Wiley, New York, Ch. 2.

Flagan, R. C., and Taylor, D. D. (1980). Laboratory studies of submicron particles from coal combustion, *Proc. 18th Symp. Combustion, Combustion Inst.*, 1227–1237.

Gladney, E. S., Small, J. A., Gordon, G. E., and Zoller, W. H. (1976). Composition and size distribution of in-stack particulate material at a coal-fired power plant, *Atmos. Environ.* 10:1071–1077.

Gluskoter, H. J., Ruch, R. R., Miller, W. H., Cahill, R. W., Dreher, G. B., and Kuhn, J. K. (1977). Trace elements in coal: Occurence and distribution, EPA Rep. 600/7-77-064, June.

Gluskoter, H. J., Shimp, N. F., and Ruch, R. R. (1981). Coal analyses, trace elements, and mineral matter, in *Chemistry of Coal Utilization* (M. A. Elliott, ed.), Wiley, New York, Ch. 7.

Gooch, J. P., and Marchant, G. H. (1978). Electrostatic precipitator rapping reentrainment and computer model studies, EPRI Rep. FP-792.

Green, H. L., and Lane, W. R. (1964). *Particulate Clouds: Dust, Smokes and Mists*, 2nd ed., Van Nostrand Reinhold, New York.

Hansen, L. D., and Fisher, G. L. (1980). Elemental distribution in coal fly ash particles, *Environ. Sci. Technol.* 14:1111–1117.

Kaakinen, J. W., Jorden, R. M., Lawasani, H. H., and West, R. E. (1975). Trace element behavior in coal-fired power plant, *Environ. Sci. Technol.* 9:862–869.

Klein D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W.S., Ogle, J. C., Talmi, Y., Van Hook, R. I., and Bolton, N. (1975). Pathways of thirty-seven trace elements through coal-fired power plant, *Environ. Sci. Technol.* 9:973–979.

Knapp, K. T. (1980). The effects of nozzle losses on impactor sampling, Paper 6, Proc. Advances in Particle Sampling and Measurement, EPA Rep. 600/9-80-004, January.

Lee, R. E., Crist, H. L., Riley, A. E., and McLeod, K.E. (1974). Concentration and size of trace metal emissions from a Power Plant, a steel plant, and a cotton gin, *Environ. Sci. Technol.* 9:643–647.

Levenspiel, O. (1962). *Chemical Reaction Engineering*, Wiley, New York.

Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., and Williams, P. (1976). Surface predominance of trace elements in airborne particles, *Science* 191:852–854.

Markowski, G. R., Ensor, D. S., Hooper, R. G., and Carr, R. C. (1980). Submicron aerosol mode in flue gas from a pulverized coal utility boiler, *Environ. Sci. Technol.*, 14:1400–1402.

McCain, J. D., Gooch, J. P., and Smith, W. B. (1975). Results of field measurements of industrial particulate sources and electrostatic precipitator performance, *J. Air Poll. Control Assoc.* 25:117–121.

McElroy, M. W., Carr, R. C., Ensor, D. S., and Markowski, G. R. (1982). Size distribution of fine particles from coal combustion, *Science* 215:13–49.

Mims, C. A., Neville, M., Quann, R. J., and Sarofim, A. F. (1979). Laboratory studies of trace element transformation during coal combustion, paper No. 78, presented 87th AIChE Meeting, August.

Neville, M., Quann, R. J., Haynes, B. S., and Sarofim, A. F. (1980). Vaporization and condensation of mineral matter during pulverized coal combustion, presented at 18th Symp. Combust., Waterloo, Canada, August.

Neville, M., Quann, R. J., Haynes, B. S., and Sarofim, A. F. (1981). Factors governing the surface enrichment on fly ash of volatile trace species, presented at the ACS/IEC Winter Symp., Tucson, AZ, January.

Ondov, J. M., Ragaini, R. C., Biermann, A. H. (1978). Elemental particle-size emissions from coal-fired power plants: Use of an internal cascade impactor, *Atmos. Environ.* 12:1175–1185.

Ondov, J. M., Ragaini, R. C., and Biermann, A. H. (1979a). Emissions and particle size distributions of minor and trace elements at two western coal-fired power plants equipped with cold-side electrostatic precipitators, *Environ. Sci. Technol.* 13:946–953.

Ondov, J. M., Ragaini, R. C., and Biermann, A. H. (1971). Elemental emissions from a coal-fired power plant. Comparison of a Venturi wet scrubber system with a cold-side electrostatic precipitator, *Environ. Sci. Technol.* 13:598–607.

Perry, R. H., and Chilton, C. H. (1973). *Chemical Engineers' Handbook*, 5th ed., McGraw Hill, New York.

Pilat, M. J. (1978). Development of a cascade impactor system, EPRI Project Rep. FP-844, August.

Ramsden, A. R. (1969). A microscopic investigation into the formation of fly ash during the combustion of a pulverized bituminous coal, *Fuel (London)* 48:121–237.

Sarofim, A. F., Howard, J. B., and Padia, A. S. (1977). The physical transformation of the mineral matter in pulverized coal under simulated combustion conditions, *Combust. Sci. Technol.* 16:187–204.

Schmidt, E. W., Gieseke, J. A., and Allen, J. M. (1976). Size distribution of fine-particulate emissions from a coal-fired power plant, *Atmos. Environ.* 10:1065–1069.

Schultz, E. J., Engdahl, R. B., and Frankenberg, T. T.

(1975). Submicron particles from a pulverized coal-fired boiler, *Atmos. Enviorn.* 9:111–119.

Shannon, L. J. (1974). Control technology for fine particulate emissions, EPA Rep. 650/2-74-027, May.

Smith, R. D. (1980). The trace element chemistry of coal during combustion and the emissions from coal-fired plants, *Progr. Energy Combust. Sci.* 6:53–119.

Smith, R. D., Campbell, J. A., and Nielson, K. K. (1979a). Concentration dependence upon particle size of volatilized elements in fly ash, *Environ. Sci. Technol.* 13:553–558.

Smith, R. D., Campbell, J. A., and Nielson, K. K. (1979b). Characterization and formation of submicron particles in coal-fired plants, *Atmos. Environ.* 13:607–617.

Stinespring, C. D., and Stewart, G. W. (1981). Surface enrichment of aluminosilicate minerals and coal combustion ash particles, *Atmos. Environ.* 15:307–313.

Swanson, V. E., Medlin, J. H., Hatch, J. R., Coleman, S. L., Wood, G. H., Woodruff, S. D., and Hildebrand, R. T. (1976). Collection, chemical analysis, and evaluation of coal samples in 1975, U.S. Geol. Survey Rep. 76-468.

Tomaides, M., and Whitby, K. T. (1975). Generation of aerosols by bursting of single bubbles, presented at Symp. Fine Particles, Minneapolis.

Ulrich, G. D., Richl, J. W., French, B. R., and Desrosiers, R. E. (1977). Mechanism of submicron fly-ash formation in a cyclone, coal-fired boiler, ASME Int. Symp. Corrosion and Desposits from Combustion Gases, Henniker, NH, June.

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EX 2A

Trace Elements in Fly Ash

Dependence of Concentration on Particle Size

144-3

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■ The concentrations of 25 elements in fly ash emitted from a coal-fired power plant have been measured as a function of particle size using spark source mass spectroscopy, optical emission spectrography, atomic absorption spectroscopy, and X-ray fluorescence spectroscopy. Of these elements, the concentrations of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr, and S were found to increase markedly with decreasing particle size. A mechanism involving high-temperature volatilization of a species containing the trace element followed by preferential condensation or adsorption onto the smallest particles is proposed to account for the trace element concentration dependence on particle size. The environmental significance of the results is discussed.

It is now well established that many high-temperature combustion and smelting operations emit particles containing toxic elements such as Be, Cd, As, Se, Pb, Sb, Hg, Tl, and V into the atmosphere (*1*). Many of these elements are enriched in ambient urban aerosols by as much as 100- to 1000-fold over their natural crustal abundance (*2*). Furthermore, most of their mass is concentrated in the particle size range 0.5–10.0 μm, which is inhaled and deposited in the human respiratory system.

A number of workers (*3–5*) have shown that inhaled airborne particles are deposited in different regions of the body depending on their aerodynamic size. This behavior is illustrated for three compartments of the respiratory system (*5*) in Figure 1. From a toxicological standpoint, the smallest particles (<1 μm) which deposit in the pulmonary region of the respiratory tract are of greatest concern. This is because the efficiency of extraction of toxic species from particles deposited in the pulmonary region is high (60–80%) (*1, 4, 6–8*), whereas the extraction efficiency from the larger particles, which deposit in the nasopharyngeal and tracheobronchial regions and are removed to the pharynx by cilial action and swallowed, is low (5–15%). Consequently, toxic species, which predominate in submicrometer-sized particles, will have their entry to the bloodstream enhanced over those which predominate in larger particles.

In fact, a number of toxic elements including Pb, Se, Sb, Cd, Ni, V, Sn, and Zn in urban aerosols have been reported to have equivalent mass median diameters of the order of 1 μm or less, which is considerably less than those reported for common matrix elements such as Fe, Al, and Si. Mass median diameters of these elements lie in the range of 2.5–7.0 μm (*9–12*). It is therefore meaningful to determine whether certain toxic elements predominate in the smallest particles emitted from particulate sources or whether the mass median diameter differences in urban aerosols are simply due to mixing of particles characteristic of individual source emissions.

The work reported here was designed to establish whether elements present in fly ash particles emitted from coal-fired power plants (essentially ubiquitous contributors to urban aerosols) exhibit a dependence of element concentration on particle size. A variety of analytical techniques was employed to choose the most reliable for the determination of individual elements in fly ash and to establish the data firmly.

Experimental

Sample Collection and Size Differentiation. Two types of samples are represented: (a) fly ash retained in the cyclonic precipitation system of a coal-fired power plant and (b) airborne fly ash collected in the ducting approximately 10 ft from the base of the stack. The retained material was collected in bulk and was size differentiated physically by sieving and aerodynamically in the laboratory with a Roller particle size analyzer (American Instrument Co.). Airborne fly ash samples were collected and size differentiated in situ using an Andersen stack sampler fabricated from stainless steel and designed to operate at the stack temperature. Although results are reported for samples collected in a single plant, the trace element content of fly ash collected in this plant equipped with cyclonic precipitators and using southern Indiana coal was shown to be representative of that in eight U.S. power plants utilizing a variety of coal types.

Particle size calibrations were based on the data supplied by the manufacturers of the analyzers employed. These data are established in terms of equivalence to the aerodynamic diameter of spherical particles of unit density (*13, 14*). Since fly ash particles are predominantly spherical, a rough check on the validity of the aerodynamic sizes can be obtained by determining the average physical size of particles in a given size fraction. For this pur-

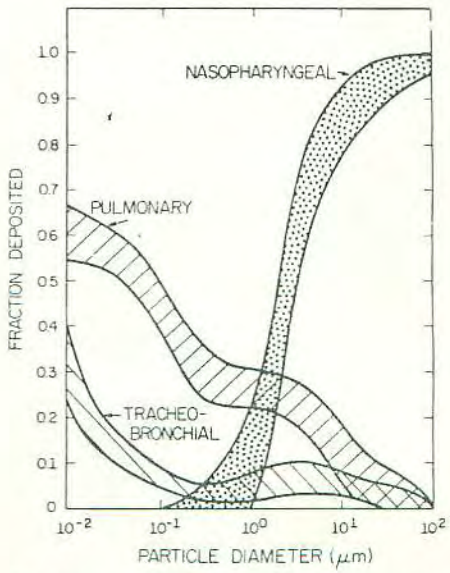

Figure 1. Efficiency of particle deposition in the three respiratory system compartments (*5*)

pose, particles collected on the third and fourth plates (4.6–7.1 μm and 3.0–4.6 μm equivalent aerodynamic diameter) of the Andersen stack sampler were examined using a Coulter counter (Coulter Electronics Inc., Hialeah, Fla.) in the timed analysis mode with a 100-μm aperture.

Milligram portions of the fly ash were dispersed in a 50% mixture of methanol in water and ultrasonically agitated for 5 min before adding the suspension to the counter. When we assumed a particle density of 2.5 g/cm^3 to convert volume median diameters to approximate aerodynamic diameters, values of 6.3 and 4.3 μm equivalent aerodynamic diameter were obtained. These indicate the general validity of the aerodynamic size calibration data.

In this experiment there was no evidence of particle diameter changing with time due to particle solubility in the methanol-water mixture. Indeed, none was expected since the particle matrices consist predominantly of insoluble aluminum and silicon and iron oxides, and soluble species are relatively minor constituents.

Analytical Procedures. The analytical methods employed fall into two classes, those which analyze the fly ash directly as the solid and those which analyze the sample in solution following wet digestion. The former methods retain sample integrity but involve calibration uncertainties; the latter allow easy calibration but are susceptible to possible formation of analytically intractable compounds during digestion.

Sample digestion was achieved by heating 0.5 gram of fly ash, 3.5 ml of 3:1 concentrated HCl/HNO_3 (aqua regia), 0.5 ml water, and 2.5 ml of an aqueous solution containing 48% HF for 2 hr at 110°C in a 25-ml Teflon-lined Parr pressure bomb (Parr Instrument Co., Moline, Ill.). After it cooled, 2.5 grams of boric acid were added to neutralize the HF. The small amount of black solid residue remaining was removed by centrifugation and was shown by spark sources mass spectrometry to contain mainly Ca, F, and Al in addition to carbon. At least 95% extraction of the elements of interest was achieved.

Atomic absorption analyses were performed by direct aspiration of dilutions of the original digest for Pb, Tl, Cd, As, Ni, and Be. Air–acetylene flames were employed for all elements except Be for which nitrous oxide–acetylene was used. A Jarrel Ash 8-10 dual-beam double monochromator instrument was employed. Background corrections were achieved by monitoring a nonabsorbing wavelength within 40 Å of the analytical wavelength. Se was determined by its atomic absorption after conversion to volatile H_2Se according to the method of Schmidt and Royer (*15*). Standard addition calibrations were performed in all cases, and a precision of ±10% was achieved.

The elements Pb, Be, Cr, Mn, Co, and Ni were determined by dc arc emission spectroscopy using a Baird-Atomic 3-meter spectrograph. Samples coarser than 325 mesh (Tyler series) were ground to pass through a 325-mesh sieve. One part by weight of fly ash was mixed with four parts of spectroscopic graphite for 1 min in a Wig-L-Bug mechanical shaker (Spex Industries). Spex mix A-7 pure graphite standards doped with 49 elements were used for comparative standards. Approximately 50 mg of graphite diluted sample were burned to completion in a cup electrode operating with a 4-mm gap and 10-amp current. Element concentrations were obtained with a precision of ±30%.

The fly ash matrix elements Fe, Ti, Al, Si, Ca, K, S, and Mg were determined using a vacuum-path, single-crystal, Phillips X-ray spectrometer. All samples of nominal particle diameter >4 μm were ground further so as to minimize surface sampling and inhomogeneity effects. The powders were suspended in propanol and dispersed ultrasonically before deposition by filtration onto 0.4-μm millipore membrane filters (*16*). Mineral standards previously calibrated against NBS mineral standards were supplied by the Illinois State Geological Survey. K_α radiation was monitored for all elements and a vacuum radiation path maintained for all elements except Fe and Ti. A lithium fluoride crystal was employed for detecting Fe and Ti, EDDT was used for Al, Si, Ca, K, and S, and ADP was used for Mg. For this method, precisions of ±5% were achieved.

An AEI model MS-7 spark source mass spectrometer was used for the qualitative determination of all elements of atomic number greater than 11 and for quantitative determination of Bi, Pb, Tl, Sb, Sn, As, Zn, Cu, Ni, Fe, V, Ca, K, and Si. One part of fly ash was mixed by weight with two parts of spectroscopic graphite for 5 min in a Wig-L-Bug and the mixture pressed into an electrode. Electrodes were manually positioned and sparked using a 25-μsec spark duration and a repetition rate of 300 sec^{-1} at 10^{-6} torr source pressure. Mass spectra were recorded photographically.

Internal standardization of the mass spectra was achieved by referencing line intensities both to the Pb in the sample and to 60 μg/g of solution-doped Au. The Pb was determined independently by atomic absorption spectroscopy. The $^{197}Au^+$ ion was at least two orders of magnitude more intense than $^{181}Ta^{16}O^+$ from source contamination. Element concentrations were calculated from the expression by Farrar (*17*).

$$C_X = C_{St} \frac{I_X}{I_{St}} \left[\frac{M_X}{M_{St}} \right]^2 \frac{\Phi_{St}}{\Phi_X} k \qquad (1)$$

where

I = peak intensity of ion beam
Φ = isotopic abundance
M = mass
C = concentration
k = sensitivity factor for a given element relative to the standard
St and X = internal standard and analyte quantities, respectively

This expression assumes that the line width on the photographic plate is proportional to $M^{1/2}$ (*18*). Values of k were determined by doping increasing amounts of Pb, Tl, Sb, Sn, As, and Ni into the graphite before forming a series of electrodes with fly ash. For these elements, values of k ranged from 1.0–1.8. For the remaining elements, k was set equal to unity, an assumption usually valid within a factor of three (*17*). Precisions of ±20% were achieved.

Carbon present as SiC, FeC, and free C was determined as CO_2 after combustion with O_2 on a V_2O_5 catalyst (*19*).

Results

Results of the fly ash analyses are listed in Tables I–III for the technique considered most reliable for each element. Sieved fly ash fractions are listed with physical diameters, but all other fractions are represented in terms of equivalent aerodynamic diameters. Fly ash particles larger than 74 μm (200 mesh, Tyler series) exhibited no dependence of element concentration on particle size so that the concentrations listed for this fraction are averages over all larger fractions.

The 25 elements are classified into three groups. In Table I are listed those elements exhibiting concentration increases with decreasing particle diameter. These concentration increases, which were well above experimental error and confirmed by at least two analytical techniques,

were consistently observed in a range of samples and were present in the airborne fly ash collected from the ducting. Table II contains elements which showed concentration trends only in the retained or in the airborne particle size fractions or which, like V, Mn, and Be, exhibited nonuniform dependence on particle size. Table III contains elements which showed no convincing trends within our experimental errors.

It should be noted that some of the values listed in Tables I–III show considerable deviation from the apparent trends. Repeated analyses of duplicate samples indicate that such deviations are essentially random and are thus

Table I. Elements Showing Pronounced Concentration Trends

Particle diam, μm	Pb	Tl	Sb	Cd	Se	As	Ni	Cr	Zn	S, wt %	Mass fraction %
	μg/g										
A. Fly Ash Retained in Plant											
Sieved fractions											
>74	140	7	1.5	<10	<12	180	100	100	500	...	66.30
44–74	160	9	7	<10	<20	500	140	90	411	1.3	22.89
Aerodynamically sized fractions											
>40	90	5	8	<10	<15	120	300	70	730	<0.01	2.50
30–40	300	5	9	<10	<15	160	130	140	570	0.01	3.54
20–30	430	9	8	<10	<15	200	160	150	480	...	3.25
15–20	520	12	19	<10	<30	300	200	170	720	...	0.80
10–15	430	15	12	<10	<30	400	210	170	770	4.4	0.31
5–10	820	20	25	<10	<50	800	230	160	1100	7.8	0.33
<5	980	45	31	<10	<50	370	260	130	1400	...	0.08
Analytical method											
	a	a	a	a	a	a	b	a	a		
B. Airborne Fly Ash											
>11.3	1100	29	17	13	13	680	460	740	8100	8.3	
7.3–11.3	1200	40	27	15	11	800	400	290	9000	...	
4.7–7.3	1500	62	34	18	16	1000	440	460	6600	7.9	
3.3–4.7	1550	67	34	22	16	900	540	470	3800	...	
2.1–3.3	1500	65	37	26	19	1200	900	1500	15000	25.0	
1.1–2.1	1600	76	53	35	59	1700	1600	3300	13000	...	
0.65–1.1	...	...	...	...	...	...	...	...	...	48.8	
Analytical method											
	d	d	d	d	d	d	d	d	a	c	

a Dc arc emission spectrometry. b Atomic absorption spectrometry. c X-ray fluorescence spectrometry. d Spark source mass spectrometry.

Table II. Elements Showing Limited Concentration Trends

Particle diameter, μm	Fe, wt %	Mn, μg/g	V, μg/g	Si, wt %	Mg, wt %	C, wt %	Be, μg/g	Al, wt %
A. Fly Ash Retained in Plant								
Sieved fractions								
>74	...	700	150	...	...	...	12	...
44–74	18	600	260	18	0.39	11	12	9.4
Aerodynamically sized fractions								
>40	50	150	250	3.0	0.02	0.12	7.5	1.3
30–40	18	630	190	14	0.31	0.21	18	6.9
20–30	...	270	340	...	...	0.63	21	...
15–20	...	210	320	...	...	2.5	22	...
10–15	6.6	160	320	19	0.16	6.6	22	9.8
5–10	8.6	210	330	26	0.39	5.5	24	13
<5	...	180	320	...	...	...	24	...
Analytical method								
	a	b	c	d	d	d		d
B. Airborne Fly Ash								
>11.3	13	150	150	34	0.89	0.66	34	19.7
7.3–11.3	...	210	240	...	...	0.70	40	...
4.7–7.3	12	230	420	27	0.95	0.62	32	16.2
3.3–4.7	...	200	230	...	...	0.57	55	...
2.06–3.3	17	240	310	35	1.4	0.81	43	21.0
1.06–2.06	...	470	480	...	...	0.61	60	...
0.65–1.06	15	...	...	23	0.19	...	...	9.8
Analytical method								
	d	b	c	d	d	e	b	d

a Dc arc emission spectrometry. b X-ray fluorescence spectrometry. c Atomic absorption. d Spark source mass spectrometry. e Oxygen fusion.

attributed to poor sampling statistics, a result of the heterogeneous nature of fly ash. It is considered appropriate, however, to present raw data obtained for a coherent set of size fractions to illustrate this problem of sampling and to avoid possible biases in the data.

Discussion

The results presented in Tables I, II, and III demonstrate four significant points:

A coal-fired power plant produces enrichment of certain elements in the smallest emitted particles.

The highest concentrations of these trace elements are found in particles which deposit in the pulmonary region of the respiratory system.

Existing particle control devices are least effective for removing the most toxic particles.

Estimates of toxic element emissions based on analyses of undifferentiated fly ash collected from particle precipitators will be much lower than actual emissions.

In fact, only a small fraction of the total fly ash mass has particle diameters <10 μm (Table I) and by no means all of this is emitted to the atmosphere. However, the fraction emitted undoubtedly presents a greater potential health hazard per unit weight than that retained. Furthermore, the dependences of element concentration on particle size presented in Table I may be less pronounced than actually occurs. This is a result of the substantial overlap of size fractions deposited on different plates of the Andersen stack sampler (*20*).

Essentially similar dependence of element concentration on fly ash particle size has been obtained by Lee and von Lehmden (*21*) for Cd, Pb, Mn, and Cr and by Toca (*22*) for Pb and Cd. Toca also found that 70% of the Cd present in flue gases was associated with particles <5 μm in diameter. More recently, Sparks (*23*) reported that the elements Pb, Ba, Sr, Rb, As, and Zn in fly ash particles collected on a 0.4-μm millipore filter, following the last stage of a Brinks impactor, were enriched on a weight-for-weight basis by at least an order of magnitude over those deposited on the last impactor stage.

One explanation of the dependence of element concentration on particle size is that the ashing characteristics of pyritic inclusions that contain many of the trace elements (*24, 25*) predominantly give rise to small particles. However, we incline to the view that certain elements or their compounds are volatilized in the high-temperature coal combustion zone and then either condense or adsorb onto entrained particles. The mass deposited is thus greatest per unit weight for the smallest particles.

In support of this volatilization adsorption–condensation hypothesis, it is noteworthy that all the elements (except Cr and Ni) listed in Table I have boiling points comparable to or below the temperature of the coal combustion zone (1300–1600°C). This is also true of Ba, Sr, and Rb as determined by Sparks (*23*). This statement implies that metal compounds are reduced to the element before volatilization. However, while reduction in the combustion zone is certainly feasible, such reduction is not necessary to our basic hypothesis. Indeed, neither Ni nor Cr, both of which exhibit a marked dependence of concentration on particle size (Table I), would exist as stable vapors (Table IV). It is suggested that these elements have access to the vapor phase as sulfides or, conceivably, as carbonyls whose highly transient formation during coal combustion has been postulated (*1*). Mercury, of course, undoubtedly volatilizes as the element and is predicted to exhibit a dependence of concentration on particle size if the proposed mechanism is valid.

Additional support for the mechanism is provided by the work of Hulett (*26*). He has shown by scanning electron microscopic analyses of individual argon ion etched fly ash particles that Zn, Cr, and Ni (the most concentrated elements in Table I) predominate on particle surfaces.

A simple model can be constructed by considering a single particle in which an element, X, is uniformly deposited on the particle surface at a concentration C_S (μg/cm^2). In addition, X is assumed to be uniformly distributed throughout the particle with a concentration C_o (μg/g). The total concentration of X, C_X (μg/g), is then given by

$$C_X = C_o + \frac{C_S A}{\rho V} \qquad (2)$$

Table III. Elements Showing No Concentration Trends

Particle diameter, μm	Bi, μg/g	Sn, μg/g	Cu, μg/g	Co, μg/g	Ti, wt %	Ca, wt %	K, wt %
A. Fly Ash Retained in Plant							
Sieved fractions							
>74	>2	>2	120	28	...	...	...
44–74	>2	>2	260	27	0.61	5.4	1.2
Aerodynamically sized							
>40	>2	>2	220	75	0.01	2.5	2.54
30–40	>2	>2	120	76	0.64	6.3	6.26
20–30	>2	>2	160	55	...	...	...
15–20	>2	>2	220	50	...	4.5	4.46
10–15	>2	>2	220	55	0.66	4.0	4.04
5–10	>2	>2	390	46	1.09	...	...
>5	>2	>2	490	54	...	...	...
B. Airborne Material							
>11.3	>1.7	7	270	60	1.12	4.9	4.9
7.3–11.3	>3.5	11	390	85	...	...	...
4.7–7.3	>4.0	18	380	90	0.92	4.2	4.2
3.3–4.7	>4.8	19	...	95	...	...	...
2.06–3.3	>4.5	16	330	90	1.59	5.0	5.0
1.06–2.06	>4.4	18	300	130	...	...	...
0.65–1.06	...	...	...	...	1.08	2.6	2.6
Analytical method							
	[a]	[a]	[a]	[b]	[c]	[c]	[c]

[a] Spark source mass spectrometry. [b] Dc arc emission spectrometry. [c] X-ray fluorescence spectrometry.

Table IV. Boiling Points of Possible Inorganic Species Evolved During Coal Combustion

Species boiling or subliming, <1550°C	Species boiling or subliming, >1550°C
As, As_2O_3, As_2S_3	Al, Al_2O_3
Ba	BaO
	BeO
Bi	Bi_2O_3
Ca	C
Cd, CdO, CdS	CaO
$Cr(CO)_6$, $CrCl_3$, CrS (155°)	Co, CoO, CoS
K	Cr, Cr_2O_3
Mg	Cu, CuO
$Ni(CO)_4$	Fe, Fe_2O_3, Fe_3O_4, FeO
$PbCl_2$, PbO, PbS	MgO, MgS
Rb	Mn, MnO, MnO_2
S	Ni, NiO
	Pb 1620–1750°C
Se, SeO_2, SeO_3	Si, SiO_2
Sb, Sb_2S_3, Sb_2O_3	Sn, SnO_2
	SrO
SnS	Ti, TiO_2, TiO
Sr	U, UO_2
Tl, Tl_2O, Tl_2O_3	
Zn, ZnS	ZnO

where

C_o = bulk concentration of X
C_S = surface concentration of X
C_X = total concentration of X
V = particle volume
A = particle surface area
ρ = particle density

By summing overall fly ash particles and assuming spherical particles, the average concentration of X, $\bar{C}_X$, is given by.

$$\bar{C}_X = \bar{C}_o + \frac{6\bar{C}_S}{\bar{\rho}} \quad \frac{1}{\bar{D}} \tag{3}$$

where D is the particle diameter and the bars denote average values. Microscopic observation does, in fact, show that most particles are spherical.

To substitute the values in Table I into Equation 3, it is necessary either to make the assumption that $\bar{\rho}$ is not a function of particle diameter, D, or to determine $\bar{\rho}$ for each size fraction. Appropriate values of D for each size fraction can be obtained by assuming

$$\bar{D} = \frac{(ECD)_u + (ECD)_l}{2} \tag{4}$$

where $(ECD)_u$ and $(ECD)_l$ are the upper and lower 50% cutoff diameters for each stage of the Andersen stack sampler. Equation 2 thus assumes a symmetrical distribution of the mass of X over the diameter range $(ECD)_u$ to $(ECD)_l$. Incorporating these assumptions enables construction of a plot of $\bar{C}_X$ vs. $\bar{D}^{-1}$ as depicted in Figure 2 from which it can be seen that the results are in at least qualitative agreement with the proposed model.

The thickness, l, of the deposition layer can then be estimated from the expression

$$l = \bar{C}_S/\bar{\rho}' \tag{5}$$

where $\bar{\rho}'$ is the density of the deposition layer which was assumed equal to 3 g/cm³. Values of $\bar{C}_S$, $\bar{C}_o$, and l are presented in Table V. These values, with the notable exception of those for sulfur, are considered reasonable for a thin surface-deposited layer. The 0.06 μm "layer thickness" obtained for sulfur is considered too great to be accounted for by a simple adsorption process. Indeed, the high concentrations of S obtained for the 0.65–1.1 μm size fraction (Table I) can only be accounted for if sulfur is present as the element. This suggestion is at variance with the findings of Hulett (27) who has shown, using electron spectroscopy, that S predominates as sulfate. We, therefore, consider that the sulfur values listed in Table I are all proportionately high owing to lack of a fly ash standard having sulfur deposited on the surface of appropriately sized particles, as required for our X-ray fluorescence analysis.

If the observed dependence of element concentration on particle size is, in fact, due to volatilization followed by adsorption or condensation, as is suggested, one would expect the same phenomenon to be exhibited by particles derived from all high-temperature solid combustion operations. Data for sources other than coal-burning power plants are not currently available to substantiate this suggestion but, if correct, it means that many sources may preferentially emit small particles high in toxic elements or their compounds. The mass median diameters of such elements in the emitted particle distribution will thus be reduced as a direct result of surface deposition. The extent of reduction can be determined by combining Equation 3 with the mass distribution function appropriate for a given particle source. In the case of a log-normal distribution, this gives the following:

$$\frac{dM_X}{d(\ln D)} = \frac{1}{\sqrt{2\pi}\ \ln \sigma_g}\left\{\bar{C}_o \exp\left[-\frac{(\ln D/D_g)^2}{2(\ln \sigma_g)^2}\right] + \frac{6C_S}{\bar{\rho}} \exp\left[\frac{(\ln \sigma_g)^2}{2}\right]\exp\left[-\frac{(\ln D/D_g + \ln^2\sigma_g)}{2\ln^2\sigma_g}\right]\right\} \tag{6}$$

where

σ_g = geometric standard deviation
M_X = mass of X
D_g = mass median diameter of original substrate distribution

Equation 6 does not provide a simple analytical expression for the mass median diameter of the adsorbed species, $D_g(X)$, except when C_o = 0—i.e., X is present only in the deposited layer. In this case, it can readily be shown (28) that

$$\ln D_g(X) = \ln D_g - \ln^2\sigma_g \tag{7}$$

Equations 6 and 7 demonstrate that the mass median diameter of a surface-deposited species, X, is considerably less than that of the total mass.

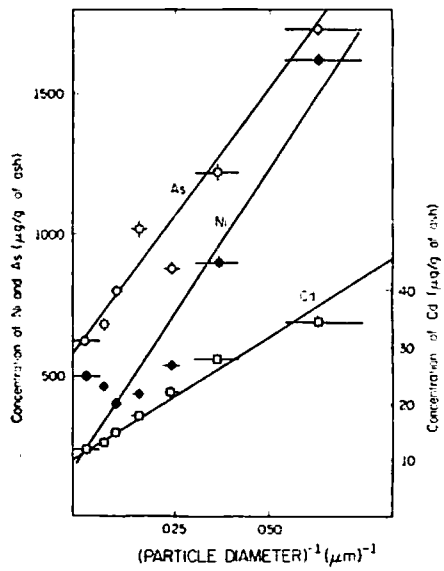

Figure 2. Dependence of element concentration on particle size for As, Ni, and Cd in fly ash emitted from a coal-fired power plant

Table V. Parameters Derived from Surface Deposition Model

Element	Sample pairs	C_s, μg/cm²	C_o, μg/g	Linear correlation coeff.	Estimated surface thickness, Å
Pb	6	0.04	1000	0.73	1.0
Tl	6	0.003	40	0.80	0.1
Sb	6	0.003	20	0.93	0.1
Cd	6	0.002	10	0.99	0.7
Se	6	0.004	0.7	0.92	0.1
As	6	0.009	600	0.97	0.3
Zn	6	0.6	6000	0.60	20
Ni	6	0.1	100	0.98	4.0
Cr	6	0.3	300	0.94	9.0
S	4	19.0	5 × 10	...	600

The validity of Equations 3 and 6 is destroyed as soon as particles from different sources become mixed into the ambient aerosol. However, if surface deposition is a widespread phenomenon as suggested earlier, one would expect volatile elements present in urban aerosols to have significantly lower mass median diameters than nonvolatile elements. In fact, data obtained by the National Air Suveillance Network (NASN) have shown the volatilizable elements Zn, Ni, Pb, Cd, and Ba to have statistically lower mass median diameters than common nonvolatilizable particle matrix elements. Also, although not substantiated statistically, Se and Sb have been shown to have small mass median diameters in ambient aerosols (*12*). Lead, of course, is not expected to be typical since it is derived mainly from a single source (the automobile) known to produce small particles.

The predominance of certain elements in small particles is also significant in determining the degree of enrichment of these elements in an urban aerosol, since the smallest particles have the longest atmospheric residence time. Indeed, Gladney et al. (*29*) have shown enrichment factors of greater than ten times over natural crustal abundance for Tl, Cr, Ni, Cu, Zn, As, Cd, Sn, Pb, Se, S, Cl, and Br in the Boston aerosol and have established substantial correlations with enrichment patterns in coal fly ash, municipal incinerator fly ash, and residual fuel oil. In the present context, it is noteworthy that the majority of these elements could be volatilized during combustion.

Although we have considered only trace elements present in particulate matter, the importance of vapor species such as SeO_2 and As_2O_3 should not be overlooked. Thermodynamic data (*30*) indicate that at 25°C as much as 80 $\mu g/m^3$ of Se as SeO_2 and 70 $\mu g/m^3$ of As as As_2O_3 can exist as vapors. These levels are much greater than normally observed for Se and As in urban aerosols ($\leq$10 ng/m^3). It is possible, therefore, that additional amounts of these elements may be emitted as vapors. Consistent with this suggestion, Pillay and Thomas (*31*) have reported that at least 50% of the Se present in urban air passes through a filter designed to collect all particles greater than 0.1 μm in diameter. Comparable data are not available for As, but future sampling operations should undoubtedly undertake gaseous sampling procedures for both elements.

By employing a variety of analytical techniques in this study it has been possible to establish which are the most reproducible, precise, and interference free for individual elements in fly ash. Spark source mass spectrometry undoubtedly affords the greatest advantage for multielemental determination in solid fly ash although the analyses are extremely time consuming. In addition, interferences prevent the analysis of Te, Cd, Se, Co, Mn, Cr, and S and permit only a semiquantitative estimate for Be. Dc arc emission spectroscopy exhibits no significant advantages over spark source mass spectroscopy other than detection of Co, Mn, Cr, and Be and wider availability. The X-ray fluorescence method employed has the advantages of high speed and precision but is somewhat limited by calibration difficulties and matrix effects. The shallow penetration depths of soft X-rays from the lighter elements such as sulfur and magnesium necessitate high matrix identity between samples and standards and a very small particle size (*32*).

Atomic absorption spectrometry is considered to be the most accurate technique employed in this work. However, large amounts of samples are required if more than a few elements are determined. Also, great care must be taken to achieve good background corrections due to the large number of elements present. Atomic absorption spectrometry displayed no evidence of loss of sample integrity as a result of the fly ash digestion except, possibly, in the case of Tl where analyses were consistently 3-5 times lower than those obtained by spark source mass spectrometry and anodic stripping voltammetry after removal of the Pb interference. The reasons for this are being investigated.

Comparison of results obtained by different techniques has enabled confirmation of the size dependences represented in Tables I-III. The absolute values of concentrations obtained by different techniques are only in semiquantitative agreement. However, this is in accord with the findings of von Lehmden et al. (*33*), who demonstrated, in a major interlaboratory comparison, that the absolute values obtained for trace elements in fly ash varied considerably between techniques and between laboratories. Nevertheless, the reproducibilities obtained for a given element using a single technique were within 10% except for occasional samples where the deviations are attributed to poor sampling statistics as discussed earlier. Since our findings and conclusions rely only on the *relative* accuracies of values obtained for different size fractions using a single technique for each element, the uncertainties in absolute accuracy are not of major consequence in this work.

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Literature Cited

(1) Schroeder, H. A., *Environment*, **13**, 18-32 (1971).
(2) Gordon, G. E., Zoller, W. H., "Normalizations and Interpretation of Atmospheric Trace-Element Concentration Patterns," Oak Ridge Trace Elements Conference, Oak Ridge, 1973.
(3) Morrow, P. E., *Amer. Ind. Hyg. Assoc. J.*, **25**, 213-36 (1964).
(4) Hatch, T. F., Gross, Paul, "Pulmonary Deposition and Retention of Inhaled Aerosols," Academic Press, New York, N.Y., 1964.
(5) United States Department of Health, Education, and Welfare, National Air Pollution Control Boards, Pub. No. AP-49, "Air Quality Criteria for Particulate Matter," Washington, D.C., January 1969.
(6) Langham, W. W., "Radioisotope Absorption and Methods of Elimination: Relative Significance of Portals of Entry," in "Symposium on Radioisotopes in the Biosphere," R. S. Caldecott and L. A. Snyder, Eds., Minneapolis, University of Minnesota Press, 1960.
(7) Patterson, C. C., *Sci. Cit.*, **10**, 66 (1968).
(8) Dautreband, L., "Microaerosols," Academic Press, New York, N.Y., 1962.
(9) Rahn, K. A., Dams, R., Robbins, J. A., Winchester, J. W., *Atmos. Environ.*, **5**, 413 (1971).
(10) Lee, R. E., Jr., Goransen, S. S., Enrione, R. E., Morgan, G. B., *Environ. Sci. Technol.*, **6**, 1025-30 (1972).
(11) Colovos, G., Wilson, G. S., Moyers, J. L., to be published in *Int. J. Environ. Anal. Chem.*, in press.
(12) Gladney, E. S., Zoller, W. H., Jones, A. G., Gordon, G. E., *Environ. Sci. Technol.*, **8**, 551-7 (1974).
(13) Ranz, W. E., Wong, J. B., *Ind. Hyg. Occupa. Med.*, **4**, 464-77 (1952).
(14) Flesch, J. P., Norris, C. H., Nugent, A. E., Jr., *Am. Ind. Hyg. Ass. J.*, **28**, 507-16 (1967).
(15) Schmidt, F. J., Royer, J. L., *Anal. Lett.*, **6** (1), 17-23 (1973).
(16) Price, N. B., Angell, G. R., *Anal. Chem.*, **40** (3), 660-3 (1968).
(17) Farrar, Harry, IV, in "Trace Analysis by Mass Spectrometry," Arthur J. Ahearn, Ed., Chap. 8, Academic Press, New York, N.Y., 1972.
(18) Owens, E. B., Giardino, N. A., *Anal. Chem.*, **35**, 1172 (1963).
(19) Steyermark, Al., "Quantitative Organic Microanalysis," p 222, Academic Press, New York, N.Y., 1961.

(20) Gordon, G. E., Director, "Study of the Emissions from Major Air Pollution Sources and Their Atmospheric Interactions, First Year Progress Report," Nov. 1, 1972-Oct. 31, 1973, University of Maryland, College Park, Md.
(21) Lee, R. E., Jr., von Lehmden, D. J., *J. Air Pollut. Contr. Ass.*, 23 (10), 853 (1973).
(22) Toca, F. M., "Lead and Cadmium Distribution in the Particulate Effluent from a Coal Fired Boiler," Ph.D. Dissertation, U. of Iowa, July 1972; see also *Diss. Abstr. Int.*, 33, 3156B (1973).
(23) Sparks, C. J., Oak Ridge National Laboratory, "Analysis of Particles Collected on a Brinks Impactor," private communication, 1973.
(24) Nicholls, G. D., in "Coal and Coal Bearing Strata," D. Merchison and P. Stanley Westoll, Eds., pp 269-307, Oliver and Boyd, London, 1968.
(25) Gluskoter, H. J., Lindahl, P. C., *Science*, 181, 264-6 (1973).
(26) Hulett, L. D., Oak Ridge National Laboratory, "Analysis of Individual Fly Ash Particles," personal communication, 1973.
(27) Hulett, L. D., *ibid.*, "The Chemical State of Sulfur in Fly Ash," personal communication, 1973.
(28) Butcher, S. S., Charlson, R. J., "An Introduction to Air Chemistry," Chap. 9, Academic Press, New York, N.Y., 1972.
(29) Gladney, E. S., Gordon, G. E., Zoller, W. H., "Abnormally Enriched Trace Elements in the Atmosphere," Seventh Annual Conference on Trace Substances in Environmental Health, U. of Missouri, Columbia, Mo., June 1973.
(30) Hodgeman, C. D., Ed.-in-chief, "Handbook of Chemistry and Physics," p 2429, 44th ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1963.
(31) Pillay, K. K. S., Thomas, C. C., Jr., *J. Radioanal. Chem.*, 7, 107-18 (1971).
(32) Muller, R. O., "Spectrochemical Analysis of X-ray Fluorescence," pp 72-86, Plenum Press, New York, N.Y., 1972.
(33) von Lehmden, D. J., Jungers, R. H., Lee, R. E., Jr., *Anal. Chem.*, 46 (2), 239 (1974).

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Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish

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■ The bioconcentration of several chemicals in trout muscle was found to follow a straight line relationship with partition coefficient. Bioconcentration in this paper is defined as the ratio of the concentration of the chemical between trout muscle and the exposure water measured at equilibrium. Partition coefficient has the usual meaning in that it is the ratio of the equilibrium concentration of the chemical between a nonpolar and polar solvent (in this case, *n*-octanol and water were the two solvents used). The relationship was established by measuring the bioconcentration in trout of a variety of chemicals over a wide range of partition coefficients. An equation of the straight line of best fit was determined and used to predict the bioconcentration of other chemicals from their partition coefficients. The predicted values agreed with the experimental values in the literature.

The ability of some chemicals to move through the food chain resulting in higher and higher concentrations at each trophic level has been termed biomagnification or bioconcentration (*1*). The widespread distributions of DDT (*2, 3*) and the polychlorinated biphenyls (PCBs) (*4*) have become classic examples of such movement. From an environmental point of view this phenomenon becomes important when the acute toxicity of the agent is low and the physiological effects go unnoticed until the chronic effects become evident. Due to the insidious nature of the bioconcentration effect, by the time chronic effects are noted, corrective action such as terminating the addition of the chemical to the ecosystem, may not take hold soon enough to alleviate the situation before irreparable damage has been done. For this reason prior knowledge of the bioconcentration potential of new or existing chemicals is desired. The importance of bioconcentration is also recognized by the Environmental Protection Agency (EPA). For example, the ability of a material to build up in the environment has become one of the proposed criteria that this regulatory agency is using in establishing toxic pollutant effluent standards (*5*).

In spite of the complexity of the reactions involved in the biomagnification process, we felt it important to see if a simple relationship could be established between the physicochemical properties of a chemical and its ability to bioconcentrate. It was our belief that the partition coefficient would be the most logical parameter to examine in this connection. If a simple relationship could be established it would be of great benefit in planning the future direction of any development work on a new chemical and in directing research efforts to determine the ultimate fate and distribution of others.

Materials and Methods

Chemicals. The following chemicals, representing a wide range of partition coefficients, were evaluated: 1,1,2,2-tetrachloroethylene, hexachlorobenzene, 2,2',4,4'-tetrachlorobiphenyl, 2-biphenylyl phenyl ether, diphenyl ether, carbon tetrachloride, and *p*-dichlorobenzene. All materials were examined for purity by means of gas chromatography and found to be >99% pure.

Bioconcentration Factor in Fish. The method described by Branson et al. (*6*) was used to determine the bioconcentration factor in rainbow trout (*Salmo gairdneri* Richardson). This method is based on determining the ratio of the concentration of the chemical in trout muscle

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EX 2B

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COMPOSITION AND SIZE DISTRIBUTION OF IN-STACK PARTICULATE MATERIAL AT A COAL-FIRED POWER PLANT

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Abstract—The particulate material in the stack effluent of a coal-fired power plant was collected and fractionated with an in-stack cascade impactor. Samples of the pulverized coal and process ashes were taken on the same days. These materials were analyzed for 34 elements by instrumental neutron and photon activation analysis. Elements on the in-stack particulates can be separated into three groups by computing enrichment factors relative to the coal for each particle size fraction. These groups are compared to proposed mechanisms for trace element fractionation during combustion.

With the increasing importance of coal as a fuel for electric power generation, there is renewed concern about the atmospheric emissions associated with coal combustion. Potentially toxic trace elements in the coal (e.g. Se, As, Hg, Pb, Sb, and Zn) may be volatilized at the temperatures encountered in the combustion zone and either redistributed onto the smaller particles entrained in the flue gas or emitted in the gas phase. The enrichment of certain trace elements on smaller particles has been discussed by Billings and Matson (1972), Billings *et al.* (1973), Gordon *et al.* (1973), Gladney *et al.* (1974), Natusch and Wallace (1974), Natusch *et al.* (1974), Kaakinen *et al.* (1975), Klein *et al.* (1975), Lee *et al.* (1975) and Ragaini and Ondov (1975). Since coal-fired generating stations are a large source of particulate material, the emission of substantial fractions of toxic trace elements on respirable particles could pose a distinct health hazard. It is important, therefore, to measure both the composition and the particle size distribution of the emitted material.

Urban particulates of dia. $\leq 1.0\ \mu m$ have unusually high enrichments of some 15 trace elements (Lee *et al.*, 1972; Gordon *et al.*, 1973; Gladney *et al.*, 1974). Sources for a few of these elements have been traced to auto emissions (Moyers *et al.*, 1972) and residual-oil combustion (Zoller *et al.*, 1973); however, sources for many of these elements remain to be identified. Careful characterization of coal-fired plant emissions should establish the importance of this source in the complex of urban emissions. Size distribution measurements may also permit the differentiation of coal-fired particulates from those of continental origin, and permit the evaluation of the former's contribution to both major- and trace-element levels observed on urban air particulates.

EXPERIMENTAL

Several varieties of cascade impactors are available for in-stack particulate sampling. The University of Washington Mark III Cascade Impactor (Pilat *et al.*, 1970) was selected as the instrument best designed to minimize wall-loss and reentrainment of collected particulates as well as having the lowest 50% effective cutoff diameter (ECD) on the final stage. This instrument can be readily attached ahead of a modified EPA sampling train (Rom, 1972; Gladney, 1974) and operated under EPA-sanctioned sampling conditions.

Impactor, pulverized coal and process ash samples were taken on several different days at the Potomac Electric Power Company's (PEPCO) Chalk Point Electric Generating Station in rural south-eastern MD. At the time of sampling the plant consisted of two 355 MW(e) generators, each consuming 10^5 kg of coal h^{-1} at full load (Berberich and Baver, 1964). The coal is ground to 50 mesh and blown from pulverizer into the furnace (water wall), and ash and flue gases are blown from the furnace through the economizer, past Cottrell electrostatic precipitators, and out two 120 m stacks. A small fraction of the coal ash (approx. 9%) is retained in the furnace and removed as bottom slag. About 12% of the ash, predominately particles of 0.1–2 mm dia., is collected at the economizer and about 75% of the ash is trapped by the precipitators and deposited in the fly ash hoppers (Reese, 1974). Approximately 4% of the total ash remains entrained in the flue gas and is emitted to the atmosphere (Whang, 1974).

The temperature of the flue gas is monitored at a number of points throughout the plant. The maximum temperature achieved in the combustion zone is 1600°C. The exhaust gas cools to 450°C during passage through the economizer. The temperatures of the inlet and outlet of the precipitator and at the base of the stack where the suspended particulates were sampled are 130, 120, and 110–120°C respectively (Reese, 1974).

The first seven stages of the Mark III impactor were covered with thin polycarbonate films that had been coated on one side with a thin layer of silicone resin. This sticky surface was employed in an effort to minimize particle bounce-off. Several different filter materials were investigated for use on the final stage of the impactor (an

Table 1. Effective cut-off diameters of mark III source test cascade impactor

Stage	ECD (μm)
1	30
2	14
3	6.0
4	2.5
5	1.4
6	0.70
7	0.35

in-line filter). Nuclepore polycarbonate filters (0.45 μm pore dia.) were selected as the best compromise among filtering capacity, blank levels, and heat resistance. This impactor has 50% ECD's shown in Table 1 when operated at a flow rate of 19.8 min^{-1} and at 130 C (Pilat *et al.*, 1973).

Ten minute isokinetic cascade impactor samples were taken using a modified EPA sampling train (details in Martin, 1971; Rom, 1972; Gladney, 1974). A 10 cm plug was designed so that an S-type Pitot tube, a pyrometer, and the impactor could be inserted in the port at the base of the stack simultaneously. The impactor would have its opening pointing "downstream" so that it could be warmed to stack temperature before sampling to avoid condensing volatiles from the gas stream during sampling. During this preheating process, the temperature and velocity of the stack gases were measured with the pyrometer and Pitot tube. These values were monitored for about 10 min, and if conditions were stable a sample was taken.

ANALYSIS

All samples were analyzed nondestructively by instrumental neutron and photon activation analyses. The analytical techniques, described in detail by Gladney (1974), were modified versions of those reported by Zoller and Gordon (1970) and Aras *et al.* (1973) for all elements except Hg. This element was measured by a combustion procedure described by Rook *et al.* (1972) on only a single impactor run. The powdered coal and fly ash were encapsulated in precleaned polyethylene vials and each impactor stage was folded and individually packaged in clean polyethylene bags. These samples were irradiated simultaneously with National Bureau of Standards (NBS) Standard Reference Materials (SRM) No. 1632 (coal) and No. 1633 (fly ash) and a solid multi-element standard prepared by pipetting a mixed elemental solution onto Whatman No. 1 filter paper. Neutron irradiations were performed at the NBS reactor at a flux of 6×10^{13} n cm^{-2} sec^{-1}, and photon irradiations were carried out at the NBS electron linac.

Spectra of the γ-rays emitted by the samples were observed several times after the various irradiations with large, high resolution Ge(Li) detectors (full-width at half maximum of 1.8 at 1332 keV) coupled to 4096-channel pulse-height analyzers. The spectra were stored on magnetic tape and the data reduced off-line by computer. Quality control of these analyses was assured by analysis of the NBS SRM's (reported in Gladney, 1974). The results for all elements compared well with data reported by Ondov *et al.* (1975) and with the NBS certified values (NBS, 1974). The uncertainties on all elemental concentration data reported in this paper are ±10%.

RESULTS AND DISCUSSION

Elemental concentrations in the coal, precipitator fly ash, and the suspended particulates are given in Table 2 for selected elements. Runs 1–3 were similar in nature and have been averaged, while individual

Table 2. Elemental concentrations in power plant materials

Element	Run	Coal (ppm)	Precip. Fly Ash (ppm)	Impactor stage (μg m^{-3}) 1	2	3	4	5	6	7	Filter	TSP*
Al	1–3	17600	130000	2300	810	1500	2300	1700	450	210	380	9600
	4	18800	135000	24	79	600	1040	810	440	52	580	3660
Na	1–3	258	2090	36	12	25	33	25	7.2	3.3	6.2	148
	4	287	2370	0.43	1.4	11	18	14	7.7	0.91	10	64
Br	1–3	42.3	6.36	0.14	0.22	0.26	0.20	0.17	0.13	0.15	0.79	2.1
	4	38.2	6.21	0.041	0.058	0.054	0.049	0.039	0.034	0.040	2.3	2.6
I	1–3	48.4	96.9	8.1	2.2	1.9	1.7	1.2	0.91	0.93	10	27
	4	52.8	131	0.72	1.1	1.3	2.2	2.6	2.7	0.36	19	30
Cr	1–3	26.3	180	3.2	1.1	2.2	3.4	2.2	0.64	0.38	1.6	15
	4	28.4	192	0.032	0.21	0.80	1.9	1.6	0.79	0.20	1.8	7.3
Ni	1–3	22.3	151	4.8	1.4	2.3	3.8	2.7	0.77	0.45	1.8	18
	4	22.0	143	0.16	0.30	1.1	2.6	1.3	0.83	0.065	1.4	7.8
Zn	1–3	27.9	229	4.7	1.8	4.0	5.1	3.8	1.0	0.63	1.3	22
	4	28.4	259	0.065	0.17	1.4	1.9	1.6	1.0	0.13	2.4	8.6
Ga	1–3	11.1	92.5	0.65	0.52	1.2	1.8	1.2	0.57	0.23	0.64	6.8
	4	13.9	81.8	0.024	0.062	0.46	0.88	0.84	0.50	0.044	0.86	3.7
As	1–3	26.0	168	6.0	3.5	8.3	12	11	5.3	3.1	32	81
	4	24.3	124	0.45	1.6	3.0	5.0	5.0	3.5	1.3	28	48
Se	1–3	3.96	23.8	3.1	3.3	3.1	1.9	0.72	0.33	0.22	1.1	14
	4	6.42	26.6	0.050	0.42	2.6	0.93	0.38	0.20	0.16	1.9	6.6
Sb	1–3	0.812	5.61	0.083	0.13	0.21	0.35	0.25	0.090	0.068	0.59	1.8
	4	1.06	7.68	0.010	0.024	0.074	0.17	0.17	0.12	0.047	0.71	1.3
Pb	1–3	10.2	59.6	1.3	1.0	2.6	2.9	2.2	0.89	0.48	3.6	15
	4	6.47	66.4	0.030	0.12	0.68	1.8	2.3	1.1	0.58	3.9	10
Hg	2	0.36	0.075	0.060	0.050	0.042	0.021	0.021	0.016	0.050	2.4	2.7

* Total suspended particulates (μg m^{-3}).

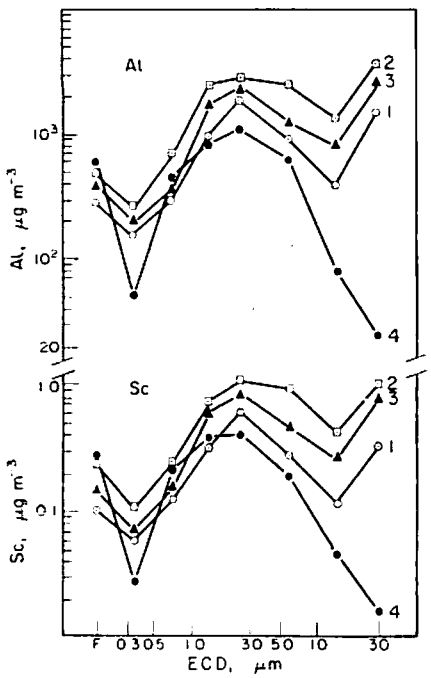

Fig. 1. In-stack size distribution of suspended particulates bearing Al and Sc at the Chalk Point Power Plant (F = backup filter)

data are presented for Run 4. Total suspended particulates are calculated by summing the concentrations across the eight impactor stages. Detailed tabular data for the 21 additional elements are reported in Gladney (1974).

Size distributions for Al, Sc, Br, and I are shown in Figs. 1 and 2. The size distributions for K, Rb, Mg, Ca, Sr, Ba, Zr, Th, Hf, Ta, V, Mn, Fe, Se, Sb, As, Ni, Cr, Co, Ti, Ga, Pb, Zn, Hg, Ce, La, Sm, Eu, Lu, and Yb were also measured, but are not shown.

The qualitative features shown by these figures are the same for all elements listed above except Hg and the halogens. Runs 1–3 usually show a higher trace element concentration on the first stage than on the second, since the particle fraction collected by the initial stage represents an integration over particle diameters greater than 30 μm. The fourth run was taken especially to get a lightly loaded sample and to avoid sampling particulates emitted as a result of "rapping" the precipitator. The rapping process removes particulates adhering to the high voltage wires in the Cottrell precipitator and results in a pulse of large diameter particulates being reentrained in the flue gas. The maximum elemental concentration occurs on particles of approx. 3 μm dia. for all four runs (except for Hg and halogens). In general, all curves, except those of Hg and the halogens, have similar shapes.

An enrichment factor, EF, for element X on each stage relative to average composition of Chalk Point Coal can be calculated using the following equation:

$$EF = ([X]_s/[\mathrm{Al}]_s)/([X]_c/[\mathrm{Al}]_c),$$

where $[X]_s$ and $[X]_c$ represent the concentrations of element X in the sample and the coal respectively, and $[\mathrm{Al}]_s$ and $[\mathrm{Al}]_c$ represent the concentrations of aluminium in the sample and the coal respectively (Gordon and Zoller, 1973). Average *EF*'s, relative to Chalk Point coal, for the fly ash and suspended particulates for runs 1–3, and individual values for run 4, are shown in Table 3. Mercury was measured only on Run 2 and the EF's reported have been calculated using Hg and Al data for the coal and fly ash collected on that day only.

When the *EF* is plotted as a function of particle size, the trace elements can be broken into at least three groups. The Na distribution depicted in Fig. 3 is typical of the first group. This distribution is almost completely featureless — the particulates have the same ratio of Na/Al as the coal across the whole size spectrum. Several elements thought to be fairly volatile (and sometimes seen at high enrichments in ambient aerosols), such as Cr, Zn, Ni, and Ga also exhibit relatively little increase in EF relative to coal. Other elements that fall into this group, and whose EF distributions have also not been shown, are K, Rb, Mg, Ca, Sr, Ba, Sc, Ti, V, Mn, Co, Zr, Th, Hf, Ta, and all rare earths except Ce.

A second group of trace elements (Pb, As, and Sb) exhibits a definite increase in *EF* on smaller particles. The As *EF* distribution shown in Fig. 4 supports the hypothesis that these elements may be condensing out of the gas phase. The Sb and Pb distributions are similar and are not shown. It is difficult to compare these observations directly with those of Natusch *et al.* (1974) since no data on coal composition and only limited data on Al concentration as a function of particle size were reported. However, the concentration

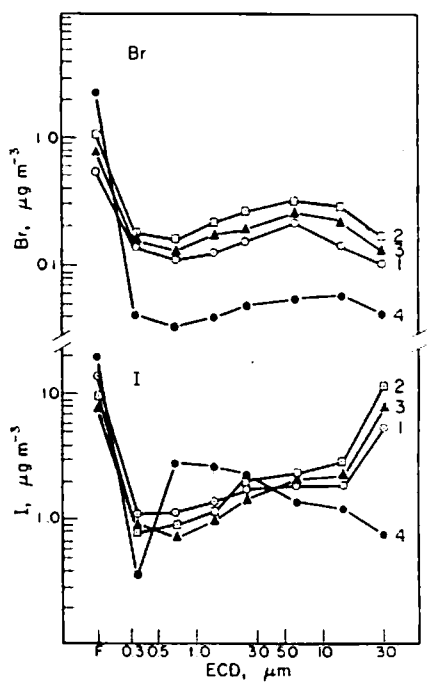

Fig. 2. In-stack size distributions of suspended particulates bearing Br and I at the Chalk Point Power Plant (F = backup filter).

Table 3. Enrichment factors of precipitator fly ash and suspended particulates relative to Chalk Point coal

Element	Run	Precip Fly Ash	Impactor stage 1	2	3	4	5	6	7	Filter	TSP*
Na	1–3	1.1	1.1	1.0	1.1	0.98	1.0	1.1	1.1	1.1	1.0
	4	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.2
Br	1–3	0.020	0.025	0.11	0.18	0.036	0.087	0.12	0.30	0.86	0.091
	4	0.023	0.84	0.36	0.044	0.023	0.024	0.038	0.38	2.0	0.36
I	1–3	0.26	1.7	1.3	0.62	0.36	1.3	1.0	2.2	13	1.4
	4	0.34	11	5.0	0.77	0.75	1.1	2.2	2.5	12	3.0
Cr	1–3	0.93	0.93	0.91	0.98	0.99	0.87	0.95	1.2	2.8	1.0
	4	0.94	0.88	1.8	0.88	1.2	1.3	1.2	2.5	2.0	1.3
Ni	1–3	0.92	1.6	1.4	1.2	1.3	1.2	1.4	1.7	3.7	1.5
	4	0.90	5.7	3.2	1.6	2.1	1.4	1.6	1.1	2.1	1.8
Zn	1–3	1.1	1.3	1.4	1.7	1.4	1.4	1.4	1.9	2.2	1.5
	4	1.3	1.8	1.4	1.5	1.2	1.3	1.5	1.7	2.7	1.6
Ga	1–3	1.1	0.45	1.0	1.3	1.2	1.1	2.0	1.7	2.7	1.1
	4	0.82	1.4	1.1	1.0	1.1	1.4	1.5	1.1	2.0	1.4
As	1–3	0.88	1.8	2.9	3.7	3.5	4.4	7.8	10	57	5.7
	4	0.71	14	16	3.8	3.7	4.8	6.0	19	37	10
Se	1–3	0.81	6.0	18	9.2	3.7	1.9	3.2	4.6	13	6.5
	4	0.58	6.1	16	13	2.6	1.4	1.3	9.0	9.6	5.4
Sb	1–3	0.94	0.78	3.5	3.0	3.3	3.2	4.3	7.0	34	4.1
	4	1.0	7.4	5.4	2.2	2.9	3.7	4.8	16	22	6.4
Pb	1–3	0.79	0.98	2.1	3.0	2.2	2.2	3.4	3.9	16	2.7
	4	1.4	3.6	4.4	3.3	5.0	8.2	7.3	30	19	8.1
Hg	2	0.028	0.31	0.80	0.46	0.12	0.16	0.55	3.1	80	17

* Total suspended particulates.

enhancement of these elements on the smaller particles at Chalk Point is less marked than that reported by Natusch *et al.* (1974) for Illinois power plants.

Selenium, Hg, Br, and I also fall in this second group, but they are especially interesting since their EF distributions differ in important detail from the other three elements. Since I and Br are bimodal and similar to Se (Fig. 5), except that enrichment on the smaller particles is more pronounced, individual figures for these two elements are not presented. Selenium and Hg (Figs. 5 and 6), two of the most volatile elements studied, would be expected to epitomize the small particle preference resulting from condensation of these elements from the gas phase. As shown in Fig. 5, this is not completely true for Se. There is an enrichment of Se on smaller particles (although not to the same extent as Pb, As, and Sb), but there is also a substantial enrichment on the largest particles with a distinct minimum in the middle-sized particles ($5.0\,\mu m \leq d \leq 0.7\,\mu m$). Mercury also

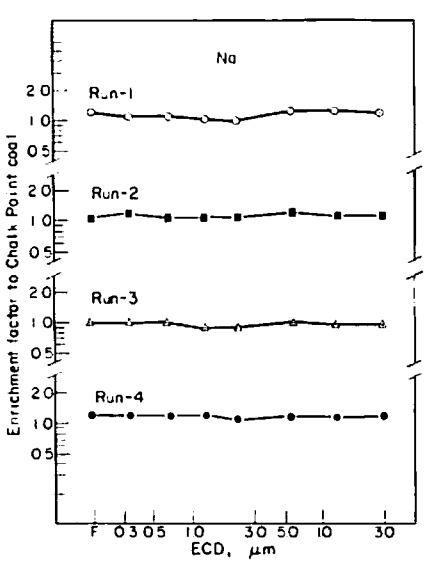

Fig. 3. Enrichment factor of Na, with respect to Chalk Point coal; as a function of in-stack particle size (F = backup filter).

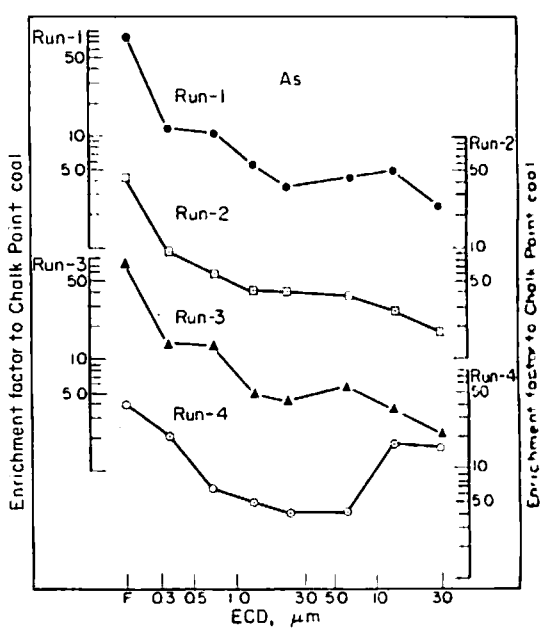

Fig. 4. Enrichment factor of As, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

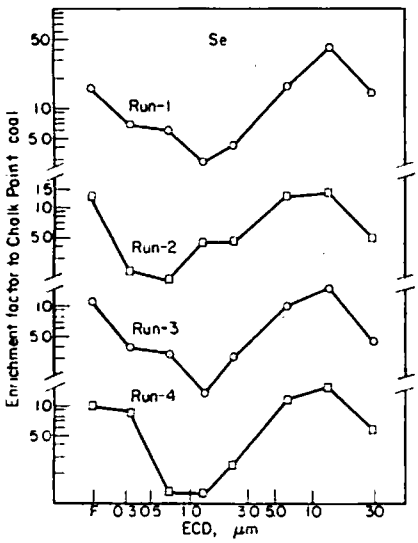

Fig. 5. Enrichment factor of Se, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

has an EF minimum in the mid-size range, but the enrichment on the smallest particles is very dramatic, which agrees with other power plant studies that focused on this element (Billings and Matson, 1972; Billings *et al.*, 1973). The model for gas phase condensation proposed by Natusch *et al.* (1974) does not adequately explain this bimodal behavior for Se, Br, I, and to a lesser extent Hg. It would be extremely useful to carefully characterize the gas phase concentrations of these elements inside the stack as an approach to explaining their peculiar distributions.

The final group of elements, consisting of Fe (Fig. 7) and Ce, exhibit a strong depletion with decreasing particle size. In the case of Fe, this might be explained by noting that most of the Fe in the coal is probably in a pyrite mineral phase (Ruch *et al.*, 1973). Since

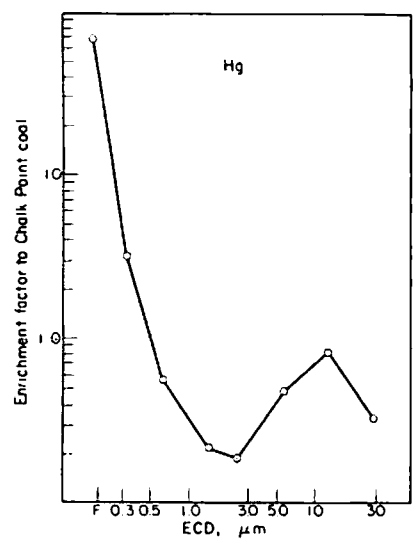

Fig. 6. Enrichment factor of Hg, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter), Run 2 only.

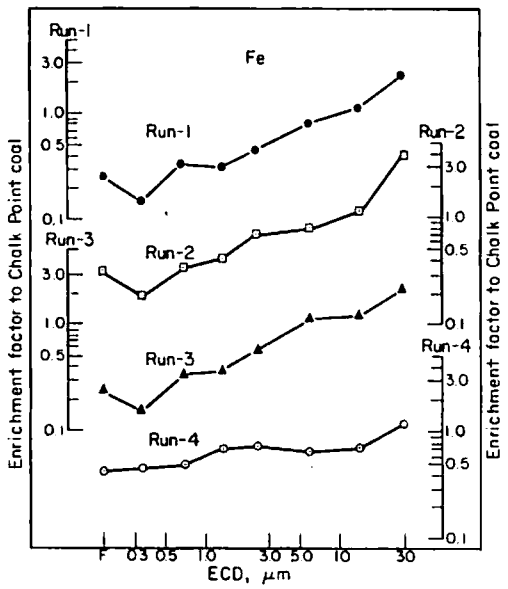

Fig. 7. Enrichment factor of Fe, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

pyrites probably behave differently from aluminosilicates during combustion, Fe might be expected to yield a rather different size distribution. Other ash fractions retained inside the plant have higher EF's for Fe than the fly ash and suspended particulates, reinforcing the idea that Fe is concentrated on the larger particles (Gladney, 1974). At the present time it is not known if Fe and Ce are associated on the same particles so that the applicability of this hypothesis for Ce cannot be determined. Cerium does not follow the Fe enrichment pattern in bottom slag and economizer ash.

Two other power plant studies (Kaakinen *et al.*, 1975; Ragaini and Ondov, 1975) present sufficient data from in-stack elemental measurements to permit a comparison. Average *EF*'s for seven elements have been calculated relative to the coal burned from these two studies and are shown in Table 4. The agreement among these three in-stack sampling efforts is reason-

Table 4. Comparison of enrichment factors for in-stack total suspended particulates*

Element	Present work†	Kaakinen *et al.*‡	Ragaini & Ondov§
As	6.8	3.1	7.3 ± 3.2
Zn	1.5	3.2	6.4 ± 4.4
Sb	4.7	3.2	6.7 ± 1.6
Se	6.2	5.7	2.5 ± 1.1
Pb	4.0	5.8	—
Ga	1.2	—	3.1 ± 0.7
Cr	1.1	—	2.0 ± 0.3

* All EF's are relative to coal burned.
† Weighted average from Table 3.
‡ Precipitator outlet stream.
§ Mean ± standard deviation for unspecified number of samples.

ably good, considering differences in sampling conditions, and power plant design and operating parameters. Zinc is definitely less enriched in the Chalk Point stack emissions, although the uncertainties in Ragaini and Ondov (1975) are high. Gallium also appears to be significantly less enriched at Chalk Point. These differences may be attributable to lower combustion and in-stack temperatures at Chalk Point. The behavior of the other elements seems to be relatively similar at the three power plants.

SUMMARY AND CONCLUSIONS

The University of Washington Mark III Cascade Impactor used in this work provided good separation of particles of different sizes as shown by the contrast in size distribution curves for different elements and by comparison with trace element size distributions from other sources (Greenberg, 1974).

Three broad classes of enrichment factor distributions for particulates have been identified. Most elements show little, if any, enrichment (compared to the input coal) as a function of particle size (e.g. Fig. 3); several of the more volatile, toxic trace elements (Sb, As, Pb, Hg, Se, Br, and I) do exhibit increased enrichments on the smaller particles; and two elements, Fe and Ce, had decreasing enrichment with decreasing particle size.

The trace elemental concentration patterns and enrichment factors as functions of particle size suggest that coal-fired power plants similar to Chalk Point, despite the emission of tons of particulate matter, do not seem to account for the high enrichment factors observed for certain particulate trace elements in cities. The nature of the trace metal emissions may be strongly influenced by the temperatures within the plant and the precipitator efficiencies at different facilities. This aspect has been discussed elsewhere (Zoller *et al.*, 1974). A number of other plants should be studied to elucidate the impact of operating conditions on the particle size distribution of the toxic trace elements. Furthermore, the gas phase components of the trace elements requires investigation.

These in-stack elemental distributions do not match the ambient particle size distributions observed for many trace elements in urban areas. Elements which are highly enriched on city aerosols (e.g. V, Zn, Se and Sb) exhibit a strong increase in concentration with decreasing particle size, with typically 50% of their elemental mass found on particles of $d \leq 1.0\,\mu m$ and *EF*'s greater than 1000 (Gladney *et al.*, 1974). The in-stack concentration distributions for all elements show distinct minima in the region $0.3 \leq d \leq 1.0\,\mu m$ and EF's of less than 100 on the smallest particles. If the differences between these distributions are observed at most coal-fired power stations, this suggests that the emissions from coal-fired installations do not have a major impact on the observed urban particle size distributions (Lee *et al.*, 1968; Nifong and Winchester, 1970; Lee *et al.*, 1972; Gladney *et al.*, 1974) for many toxic trace elements.

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REFERENCES

Aras N. K., Zoller W. H., Gordon G. E. and Lutz G. J. (1973) Instrumental photon activation analysis of atmospheric particulate material. *Analyt. Chem.* **45**, 1481–1490.

Berberich C. E. and Baver C. B. (1964) Design features of the Chalk Point Generating Station. Presented at Southeastern Electric Exchange, Washington, D.C.

Billings C. E. and Matson W. R. (1972) Mercury emissions from coal combustion. *Science* **176**, 1232–1233.

Billings C. E., Sacco A. M., Matson W. R., Griffin R. M., Coniglio W. R. and Harley R. A. (1973) Mercury balance on a large pulverized coal-fired furnace. *J. Air Pollut. Control Ass.* **23**, 773–777.

Gladney E. S. (1974) Trace element emissions from coal-fired power plants: A study of the Chalk Point Electric Generating Station. Ph.D. Thesis, University of Maryland.

Gladney E. S., Zoller W. H., Jones A. G. and Gordon G. E. (1974) Composition and size distribution of atmospheric particulate matter in the Boston area. *Environ. Sci. Technol.* **8**, 551–557.

Gordon G. E., Zoller W. H. and Gladney E. S. (1973) Abnormally enriched trace elements in the atmosphere. *Trace Substances in Environmental Health VII* (Edited by Hemphill D. D.), pp. 167–174. University of Missouri, Columbia, MO.

Gordon G. E. and Zoller W. H. (1973) Normalization and interpretation of atmospheric trace element concentration patterns. *Proc. 1st Annual NSF Trace Contaminants Conference*, Oak Ridge National Laboratory, Oak Ridge, Tenn., CONF-730802, pp. 314–325.

Greenberg R. R. (1974) University of Maryland, private communication.

Kaakinen J. W., Jorden R. M., Lawasani M. H. and West R. E. (1975) Trace element behavior in coal-fired power plant. *Environ. Sci. Technol.* **9**, 862–869.

Klein D. H., Andren A. W., Carter J. A., Emery J. F., Feldman C., Fulkerson W., Lyon W. S., Ogle J. C., Talmi Y., Van Hook R. I. and Bolton N. (1975) Pathways of thirty-seven elements through coal-fired power plant. *Environ. Sci. Technol.* **9**, 973–979.

Lee R. E., Patterson R. K. and Wagman J. (1968) Particle size distribution of metal components in Urban air. *Environ. Sci. Technol.* **2**, 288–290.

Lee R. E., Goranson S., Enrione R. and Morgan G. (1972) The NASN cascade impactor network—II. Size distributions of trace metal components. *Environ. Sci. Technol.* **6**, 1025–1030.

Lee R. E., Crist, H. L., Riley A. E. and MacLeod K. E. (1975) Concentration and size of trace metal emissions from a power plant, a steel plant, and a cotton gin. *Environ. Sci. Technol.* **9**, 643–647.

Martin R. M. (1971) Construction details of isokinetic source-sampling. equipment. Air Pollution Control Office, EPA, Research Triangle Park, N.C., Pub. No. APTD-0581.

Moyers J. L., Zoller W. H., Duce R. A. and Hoffman G. L. (1972) Gaseous bromine and particulate lead, vanadium and bromine in a polluted atmosphere. *Environ. Sci. Technol.* 6, 68–71.

National Bureau of Standards (1974) Certificate of Analysis. Standard Reference Material No. 1632 (Coal), Washington, D.C.

National Bureau of Standards (1974) Certificate of Analysis. Standard Reference Material No. 1633 (Coal Fly Ash), Washington, D.C.

Natusch D. F. S., Wallace J. R. and Evans C. A. (1974) Toxic trace elements: preferential concentration in respirable particles. *Science* 183, 202–204.

Natusch D. F. S. and Wallace J. R. (1974) Urban aerosol toxicity: the influence of particle size. *Science* 186, 695–699.

Nifong G. D. and Winchester J. W. (1970) Particle size distributions of trace elements in polluted aerosols. University of Michigan, Report C001705B.

Ondov J. M., Zoller W. H., Olmez I., Aras N. K., Gordon G. E., Rancitelli L. A., Abel K. H., Filby R. H., Shag K. R. and Ragaini R. C. (1975) Elemental concentrations in the NBS environmental coal and fly ash standard reference materials. *Analyt. Chem.* 47, 1102–1109.

Pilat M. J., Ensor D. S. and Bosch J. C. (1970) Source test cascade impactor. *Atmospheric Environment* 4, 671–679.

Pilat M. J., Ensor D. S. and Shattenburg G. E. (1973) *Operation Manual for Mark III University of Washington Source Test Cascade Impactor.*

Ragaini R. C. and Ondov J. M. (1975) Trace contaminants from coal-fired power plants. International Conference on Environmental Sensing and Assessment, Las Vegas, NV.

Reese C. (1974) Plant Manager, Chalk Point, Potomac Electric Power Co., private communication.

Rom J. J. (1972) Maintenance, calibration, and operation of isokinetic source-sampling equipment. Office of Air Programs, EPA, Research Triangle Park, N.C., Pub. No. APTD-0576.

Rook H. L., Gills T. E. and LaFleur P. D. (1972) Method for determination of mercury in biological materials by neutron activation analysis. *Analyt. Chem.* 44, 1114–1117.

Ruch R. R., Gluskoter H. J. and Shimp H. F. (1973) Occurrence and distribution potentially volatile trace elements in coal: An interim report. Environmental Geology Notes Vol. 61. Illinois Geological Survey, Urbana, IL.

Whang J. S. (1974) Real-time characterization of particulates emitted by a coal-fired power plant. Ph.D. Thesis, University of Maryland.

Zoller E. H. and Gordon G. E. (1970) Instrumental neutron activation analysis of atmospheric pollutants utilizing Ge(Li) gamma-ray detectors. *Analyt. Chem.* 42, 257–265.

Zoller W. H., Gordon G. E., Gladney E. S. and Jones A. G. (1973) The sources and distribution of vanadium in the atmosphere. In *Geochemical Cycles of Trace Elements in Our Environment* (Edited by Kothny E. L.). *Advances in Chemistry Series* pp. 31–47. No. 123. American Chemical Society, Washington, D.C.

Zoller W. H., Gladney E. S., Gordon G. E. and Bors J. J. (1974) Emissions of trace elements from coal-fired power plants. In *Trace Substances in Environmental Health VIII* (Edited by Hemphill D. D.). Vol. 8, pp. 167–172. University of Missouri, Columbia, MO.

EX 2C

Eng., 90, 79–107 (1964).
(27) Adamson, A. W., "Physical Chemistry of Surfaces", 2nd ed., Interscience, New York, 1967, p 573.
(28) Lemieux, R., Morrison, J., *Can. J. Res.*, 25B, 212 (1947).
(29) Zechmeister, L., "Progress in Chromatography", Wiley, New York, 1950, p 189.
(30) Weber, W. J., Jr., van Vliet, B. M., presented at the 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 10–15, 1978.
(31) Liapis, A. I., Rippin, D. W. T., *Chem. Eng. Sci.*, 32, 619 (1977).
(32) Butler, J. A. V., Ockrent, C. J., *J. Phys. Chem.*, 34, 2841 (1930).
(33) Jain, J. S., Snoeyink, V. L., *J. Water Pollut. Control Fed.*, 45, 2463–79 (1973).
(34) Radke, C. J., Prausnitz, J. M., *AIChE J.*, 18, 761–8 (1972).
(35) Jossens, L., Prausnitz, J. M., Fritz, W., Schunder, E. U., Myers, A. L., *Chem. Eng. Sci.*, 33, 1097 (1978).
(36) Myers, A. L., Prausnitz, J. M., *AIChE J.*, 11, 121 (1965).
(37) DiGiano, F. A., Baldauf, G., Frick, B., Sontheimer, H., *Chem. Eng. Sci.*, 33, 1667–73 (1978).
(38) Manes, M., presented at the 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 10–15, 1978.
(39) Hofer, L. J. E., Manes, M., *Chem. Eng. Prog.*, 65, 84 (1969).
(40) Manes, M., Hofer, L. J. E., *J. Phys. Chem.*, 73, 584 (1969).
(41) Wohleber, D. A., Manes, M., *J. Phys. Chem.*, 75, 61 (1971).
(42) Wohleber, D. A., Manes, M., *J. Phys. Chem.*, 75, 3720 (1971).
(43) Rosene, M. R., Ozcan, M., Manes, M., *J. Phys. Chem.*, 80, 2586 (1976).
(44) McGuire, M. J., Suffet, I. H., Radzail, J. V., *J. Am. Water Works Assoc.*, 70, 565 (Oct 1978).
(45) McGuire, M. J., Ph.D. Thesis, Drexel University, Philadelphia, 1977.
(46) Keller, R. A., Snyder, L. R., *J. Chromatog. Sci.*, 9, 346 (1971).
(47) Sinanoglu, O., in "Molecular Associations XIN Biology", Pullman, B., Ed., Academic Press, New York, 1968, pp 427–45.
(48) Sinanoglu, O., Abdulnur, S., *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, 24, No. 2, Part III, S-12 (1965).
(49) Halicioglu, T., Sinanoglu, O., *Ann. N.Y. Acad. Sci.*, 158, 308 (1969).
(50) Horvath, C., Melander, W., Molnar, I., *J. Chromatogr.*, 125, 129 (1976).
(51) Aberhalden, E., Foder, A., *Fermentforschung*, 2, 74, 151 (1910).
(52) Cheldin, V. H., Williams, R. J., *J. Am. Chem. Soc.*, 64, 1513 (1942).
(53) Tiselius, A., Ed., The Svedberg, Almquist and Wiksells, Upsala, 1944, p 370.
(54) Williams, R. J. P., Hagdahl, L., Tiselius, A., *Ark. Kemi*, 7, 1 (1954).
(55) Colin, H., Eon, C., Guiochon, G., *J. Chromatogr.*, 119, 41 (1970).
(56) Colin, H., Eon, C., Guiochon, G., *J. Chromatogr.*, 122, 223 (1976).
(57) Colin, H., Guiochon, G., *J. Chromatogr.*, 137, 19 (1977).
(58) Colin, H., Ward, N., Guiochon, G., *J. Chromatogr.*, 149, 169 (1978).
(59) Colin, H., Guiochon, G., *J. Chromatogr.*, 158, 183 (1978).
(60) Horvath, C., Melander, W., Molnar, I., *Anal. Chem.*, 49, 142 (1977).
(61) Horvath, C., Melander, W., *Am. Lab.*, 10, 17 (1978).
(62) Franks, H. S., Evans, M. W., *J. Chem. Phys.*, 13(11), 507 (1945).
(63) Kauzmann, W., *Adv. Protein Chem.*, 14, 1 (1959).
(64) Tanford, C., *Science*, 200, 1012 (1978).
(65) Sourirajan, S., Matsuura, T., "Reverse Osmosis and Synthetic Membranes", Sourirajan, S., Ed., National Research Council Canada, Ottawa, Canada, 1977, pp 5–43.
(66) Barrow, G. M., *J. Phys. Chem.*, 59, 1129 (1955).
(67) Gordy, W., *J. Chem. Phys.*, 7, 93–9 (1939).
(68) Gordy, W., Stanford, S. C., *J. Chem. Phys.*, 8, 170–7 (1940).
(69) Gordy, W., Stanford, S. C., *J. Chem. Phys.*, 9, 204–14 (1941).
(70) Gordy, W., *J. Chem. Phys.*, 9, 215–23 (1941).
(71) Kuhn, L. P., *J. Am. Chem. Soc.*, 74, 2492–9 (1952).
(72) Kagija, T., Sumida, Y., Inoue, T., *Bull. Chem. Soc. Jpn.*, 41, 767 (1968).
(73) Taft, R. W., Jr., in "Steric Effects in Organic Chemistry", Newman, M. S., Ed., Wiley, New York, 1956, pp 556–675.
(74) Hammett, L. P., "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, pp 347–90.
(75) Pinsky, J., *Mod. Plast.*, 34(4), 145 (1957).
(76) Diamond, J. M., Wright, E. M., *Annu. Rev. Physiol.*, 31, 581–646 (1969).

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Emissions and Particle-Size Distributions of Minor and Trace Elements at Two Western Coal-Fired Power Plants Equipped with Cold-Side Electrostatic Precipitators

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■ Concentrations and distributions according to particle size of up to 42 elements were measured in aerosol particles collected in-stack at two western coal-fired power plants equipped with cold-side electrostatic precipitators (ESP). Elements were measured by instrumental neutron activation analysis, atomic absorption spectroscopy, and X-ray fluorescence. Particle-size distributions in filter and cascade impactor samples from both units were bimodal. Most of the particulate material from the units was emitted as large particles with mass median aerodynamic diameters of $>1.6\ \mu m$. Emission rates normalized per joule of input heat strongly reflect differences in the type and efficiency of the control devices and the chemistry of the coal. However, the relative penetrations of many elements at both plants were remarkably similar despite major differences in coal composition and plant design. Our results are compared with those of three other studies of similarly equipped power plants. Relative penetrations of Zn, Pb, Ba, Cr, Co, V, Rb, and Sb differed significantly among the five plants.

The National Coal Association forecasts an increase in utility coal usage from 4.0×10^{11} kg in 1976 to approximately 7.7×10^{11} kg in 1985. The nation's expanding reliance on coal combustion in the production of electric power has increased the importance of evaluating the associated potential biomedical and environmental hazards. Coal combustion results in the release into the atmosphere of a number of potentially toxic substances, including naturally occurring radionuclides (*1–5*), polynuclear aromatic hydrocarbons (*6–8*), and various inorganic chemical species (*9–16*), in vapor (*16, 17*) and condensed phases.

Several investigators have studied the behavior of trace elements during coal combustion. Davison (*18*) proposed a mechanism whereby volatile species are enriched in respirable, fine particles through vaporization in the combustion zone followed by condensation on particle surfaces. Kaakinen et al. (*9*) and Klein et al. (*11*) demonstrated enrichment of elements in emitted particles resulting from the greater penetration of fine, highly enriched particles through emission control devices. Others (*1, 12, 14, 15, 18*) observed similar

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enrichments by these mechanisms in small particles emitted from coal combustion. However, comprehensive studies of trace element emissions from the combustion of U.S. coal have been reported for only a few utility-scale generating units. These include Unit No. 5 of the Valmont Power Station (*9*), the T. A. Allen Steam Plant (*11*), and the Chalk Point Plant (*12*). Most of the plants studied burn Eastern and Illinois coals, and relatively few studies have been made of plants burning low-sulfur, Western coal. Thus, in general, the specific effects on emissions of coal type, differences in the chemical form and physical distribution of coal constituents, and emission-control devices have not been adequately determined.

Furthermore, insufficient attention has been given to measuring particle-distribution parameters, especially in submicrometer particles. The emission of fine particles is of special interest because these particles often contain high concentrations of potentially toxic substances in thin, surface layers (*19*) and can be deposited efficiently in the pulmonary alveoli (*20*).

In this paper, we report the results of tests on power units at two conventional, large, western, coal-fired power plants (referred to as plants A and B), one burning low-sulfur bituminous coal, the other burning low-sulfur subbituminous coal. Cold-side electrostatic precipitators (ESP) were used to control particulate emissions at both plants.

Experimental

Plant Description and Sample Collection. At plant A, we tested a 430-MW (net electrical) coal-fired steam electric generator. The unit uses tangentially fired burners and a cold-side ESP with an efficiency between 99.5 and 99.8%. The unit burns $\sim 1.45 \times 10^5$ kg of pulverized (200-mesh) western bituminous coal per hour, with ash, sulfur, and heat contents of 9.2%, 0.46%, and 28660 J/g, respectively, on a dry basis (moisture content was 6.8%). Stack gases exit through a 183-m stack.

Four filter and seven impactor samples were collected isokinetically in stack at the 91-m level during a 1-week period in January 1975. Sampling times ranged from 55 min to 3 h, the stack temperature was 117 °C, stack pressure ranged from 1.12 to 1.87 mmHg (gauge), and stack-gas velocity ranged from 23.9 to 25.9 m/s. Velocity-traverse data showed that the velocity profile was flat 91 cm beyond the inside wall. Flow rates through both impactor and filter samplers ranged from 10.8 to 16.1 L/min (wet gas volume).

At plant B, the 750-MWe ESP-equipped unit uses opposed front- and rear-fired burners. Flue gases leaving the boiler flow through two cold-side ESPs arranged in a chevron design before exiting through a 91-m stack. Each precipitator is four units wide and four mechanical sections long and has a specific collecting area of 4760 cm^2/m^3. When all sections are operating properly, net particle-removal efficiency of the ESP system at full load is rated at 97%.

Samples were collected in-stack at the 61-m level of the ESP-equipped unit during July 1975 (*21*). The gross load varied from 515 to 715 MWe, but was constant during each test. Four of the 32 separate electrical precipitator sections were inoperative during most of the test period. Precipitator efficiency in removing total suspended particles (TSP) under the test conditions was estimated at about 97% (see below). Eight filter and ten cascade impactor samples were collected. Additional samples, including simultaneous samples from the inlet, outlet, and plume (*15*), were collected during February 1976, but are not reported here.

Samples of coal, ESP-collected ash, and bottom ash were also taken at both plants during stack fly-ash collections. At plant A, pulverized coal samples were taken hourly, each sample consisting of a 5-min sample from each of five feeding systems.

Sampling Procedures. Stack emissions were sampled at each plant, using a modified EPA sampling train as described previously (*22*). Hourly records of plant operating data, including gross generating load, coal consumption, proximate analyses, energy-conversion factors (daily at plant A, monthly at plant B), and status of ESP sections, were obtained at both plants. Velocity, temperature, and pressure of the stack gas were monitored continuously during each collection. Filter samples were collected on 47-mm, 0.4-μm Nuclepore filters. Impactor samples were collected with 7- and 11-stage University of Washington Mark III and Mark V source test cascade impactors, using polyethylene or polycarbonate collection substrates and 47-mm, 0.4-μm Nuclepore backup filters. Impaction substrates were coated with a vacuum grease to improve the collection efficiency.

Analyses. In addition to gravimetric analyses, up to 43 elements were analyzed in stack samples, ESP-collected ash, bottom ash, and coal by instrumental neutron activation analysis (INAA) as described previously (*23, 24*). Cadmium and Be were analyzed in coal and fly ash, and Pb, Cd, and Be were analyzed in filter and cascade impactor samples, all with a Perkin-Elmer Model 603 atomic absorption spectrometer equipped with a Perkin-Elmer Model 2100 heated graphite analyzer. Samples were dissolved in a mixture of perchloric, nitric, and hydrofluoric acids after ashing overnight at 450 °C. Mercury in coal was analyzed by flameless atomic absorption techniques similar to those of Murphy (*25*). Nickel, Pb, and Cd were measured in bulk coal and fly-ash samples with energy-dispersive X-ray fluorescence analyses (XRF). Coal samples for XRF were dry ashed at 450 °C overnight, ground to 30 to 60 μm, and pressed into pellets with an equal amount of Avicel binding agent. γ rays from ^{109}Cd were used to excite characteristic fluorescent X-rays. The measurement and analyses of spectra are described by Bonner et al. (*26*). Results from each of these techniques were verified with NBS standard reference materials (SRM) 1632 (coal) and 1633 (coal fly ash), which were analyzed along with the samples, and through interlaboratory comparisons of results on SRM samples (*27*) and size-classified fly-ash fractions (*28*).

Computation of Coal Consumption and Atmospheric Discharge Rates. Rates of coal consumption were computed from data provided by plant personnel. At plant A, the coal consumption rate was measured by the plant-metering system and at plant B it was computed from the gross electrical generating load, the known heat-to-electrical conversion factor (a monthly average), and the heat content of the coal as described previously (*21*). Input rates of constituent elements were obtained by multiplying their concentrations in coal (listed in Table I) by the rate of coal consumption. Typical rates of coal consumption at each of the units are listed in Table II.

Rates of atmospheric discharge of minor and trace element species were computed using the measured stack concentrations and stack-gas velocities. Because the quantities of coal consumed, electric power produced, and energy-conversion factors of the units differed, comparison of the emission data is facilitated by normalizing the data to the amount of heat input into the boiler. The heat input was computed from the metered coal-flow rate and the heat content of the coal for the unit at plant A and from the gross generating load and energy-conversion factor for the unit at plant B. The energy-conversion factors are listed in Table II.

Results and Discussion

Distributions of Total Suspended Particles. Parameters used to calculate the total aerosol emitted from each of the two plants were obtained by counting particles on filter samples

Table I. Concentrations of Elements in Coal Burned at Two Western Power Plants, μg/g

	Plant A	Plant B	
	Jan 75	July 75	Feb. 76
Al	7072 ± 360 (5)[a]	30300 ± 3600 (15)[a]	29500 ± 2390 (7)[a]
Ag	0.250 ± 0.026 (1)	–	–
As	0.583 ± 0.087 (12)	2.73 ± 0.71 (11)	2.84 ± 0.84 (5)
Ba	78.5 ± 9.2 (12)	418 ± 88 (14)	420 ± 167 (7)
Be[b]	0.32 ± 0.11 (6)	1.6 ± 0.5 (9)	1.2 ± 0.6 (7)
Br	–	0.96 ± 0.18 (2)	–
Ca	6100 ± 470 (5)	5360 ± 730 (15)	5620 ± 860 (7)
Cd[b]	0.14 ± 0.025 (5)	0.061 ± 0.019 (10)	0.17 ± 0.02 (7)
Ce	8.93 ± 0.22 (12)	25.6 ± 1.7 (15)	27.0 ± 2.0 (7)
Cl	73 ± 18 (5)	71 ± 20 (4)	48 ± 17 (1)
Co	0.840 ± 0.040 (12)	1.98 ± 0.25 (14)	2.08 ± 0.22 (7)
Cr	7.74 ± 0.33 (12)	5.19 ± 0.29 (15)	7.02 ± 1.28 (7)
Cs	0.454 ± 0.012 (5)	0.70 ± 0.08 (15)	0.72 ± 0.16 (7)
Cu	6.68 ± 0.22 (5)	13.4 ± 1.2 (6)	12.7 ± 0.6 (7)
Dy	0.54 ± 0.02 (5)	1.63 ± 0.13 (15)	1.60 ± 0.09 (7)
Eu	0.101 ± 0.005 (5)	0.250 ± 0.009 (14)	0.261 ± 0.018 (7)
Fe	2860 ± 120 (12)	5720 ± 380 (15)	6470 ± 570 (7)
Ga	2.67 ± 0.50 (12)	8.8 ± 1.4 (11)	8.48 ± 1.25 (7)
Hf	1.14 ± 0.10 (5)	2.23 ± 0.12 (15)	2.38 ± 0.11 (7)
Hg	0.11 ± 0.01 (5)	0.065 ± 0.015 (5)	0.10 ± 0.02 (5)
In	0.010 ± 0.002 (3)	0.0415 ± 0.0046 (13)	0.039 ± 0.006 (5)
K	764 ± 45 (5)	1820 ± 250 (14)	1730 ± 261 (7)
La	5.09 ± 0.34 (5)	14.3 ± 0.8 (15)	13.4 ± 0.8 (7)
Lu	0.062 ± 0.015 (5)	0.239 ± 0.009 (14)	0.23 ± 0.03 (6)
Mg	1025 ± 109 (5)	2330 ± 470 (11)	2240 ± 753 (6)
Mo	1.17 ± 0.05 (5)	2.60 ± 0.54 (15)	2.67 ± 0.26 (6)
Mn	13.3 ± 3.4 (9)	54.1 ± 1.6 (15)	60.2 ± 20.0 (7)
Na	2330 ± 70 (5)	2940 ± 160 (15)	2930 ± 248 (7)
Nd	3.98 ± 0.20 (5)	9.86 ± 0.90 (15)	10.6 ± 1.1 (7)
Ni[c]	2.99 ± 0.45 (5)	–	–
Pb[c]	2.52 ± 0.13 (5)	10.2 ± 1.2 (16)	12.1 ± 0.7 (7)
Rb	4.03 ± 0.32 (5)	9.05 ± 0.53 (15)	12.1 ± 1.8 (7)
Sd	4600 ± 100 (5)	5200 ± 800 (2)	5800 ± 600 (12)
Sb	0.160 ± 0.011 (5)	0.572 ± 0.049 (15)	0.614 ± 0.095 (7)
Sc	1.46 ± 0.09 (12)	2.77 ± 0.11 (15)	2.98 ± 0.20 (7)
Se	1.47 ± 0.09 (12)	1.55 ± 0.15 (15)	1.74 ± 0.25 (7)
Sm	0.659 ± 0.013 (12)	1.71 ± 0.17 (15)	1.81 ± 0.16 (7)
Sr	67.0 ± 2.7 (5)	87.2 ± 8.9 (15)	97.7 ± 8.3 (7)
Ta	0.160 ± 0.006 (5)	0.492 ± 0.038 (15)	0.513 ± 0.056 (7)
Tb	0.0810 ± 0.003 (5)	0.165 ± 0.009 (15)	0.22 ± 0.02 (7)
Th	1.65 ± 0.03 (5)	5.73 ± 0.32 (15)	6.21 ± 0.67 (7)
Ti	483 ± 82 (5)	1220 ± 200 (14)	1230 ± 176 (6)
U	0.573 ± 0.023 (5)	1.85 ± 0.19 (15)	2.12 ± 0.25 (7)
V	9.8 ± 1.2 (12)	22.1 ± 3.2 (9)	24.9 ± 3.1 (4)
W	–	0.80 ± 0.24 (5)	<0.13 (1)
Yb	0.368 ± 0.022 (5)	0.817 ± 0.060 (15)	0.84 ± 0.06 (7)
Zn	7.16 ± 0.29 (5)	14.7 ± 1.7 (15)	16.4 ± 3.2 (7)
Zr	40.5 ± 6.5 (5)	52.2 ± 5.9 (15)	66.7 ± 9.8 (7)

[a] Number of replicate samples. [b] Measured by atomic absorption spectroscopy. [c] X-ray fluorescence. [d] Sulfur analyses provided by plant personnel; all others measured by instrumental neutron activation analysis.

Table II. Typical Rates of Coal Consumption and Energy-Conversion Factors

	% Full load	Coal rate (g/s)	Energy-conversion factor (Btu/kWh)
Plant A	98	3.98×10^4	9.25×10^3
Plant B	94	9.71×10^4	9.47×10^3
	82	8.57×10^4	9.38×10^3

Table III. Size-Distribution Parameters of Total Stack-Emitted Aerosols Determined from Scanning Electron Microscopy Analyses of Nuclepore Filter Samples

	Small-Particle Mode				Large-Particle Mode			
	NMD[a]	VMD[b]	MMAD[c]	σ_g[d]	NMD[a]	VMD[b]	MMAD[c]	σ_g[d]
Plant A	0.065	0.088	0.14	1.37	0.565	1.04	1.6	1.57
Plant B	0.056	0.084	0.13	1.42	0.74	5.2	8.1	2.2

[a] Number median diameter (μm). [b] Volume median diameter (μm) determined by $\ln VMD = \ln NMD + 3 \ln^2 \sigma_g$. [c] Estimated mass median aerodynamic diameter (μm), using particle densities of 2.2 and 2.44 g/cm³ for plants A and B, respectively. [d] Geometric standard deviation of assumed log normal distribution.

via scanning electron microscopy (SEM) techniques (see ref 22) and are given in Table III. The distributions were in each case bimodal, with distinct modes in sub- and supermicrometer size ranges. The submicrometer mode is composed of aggregates of smaller particles that may be formed in part from vapor condensation and bubble-bursting mechanisms. These particles are too small to be collected by our impactor and, ignoring wall losses and boundary effects in the impactor, are deposited totally on the backup filter. The second mode contains much larger, mostly solid, spherical particles derived mainly from residual mineral matter in coal (*29–31*). Urlich (*30*) observed similar particle-distribution modes and suggested that the particles in the smaller mode are largely condensed, volatile Si compounds and metal oxides.

Median diameters of the smaller particles from both units are almost identical. Median diameters of the larger particles (see Table III) strongly reflect differences in the overall collection efficiency of the control device. The smaller median diameters of the large particles emitted at plant A indicate a greater collection efficiency of the larger particles. Optimum collection efficiencies of the plant A and plant B ESP systems are 99.7 and 97.5%, respectively.

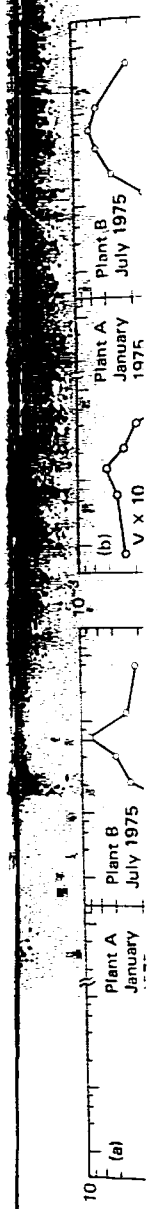
Impactor Data. In Figures 1A through E, we have plotted typical particle-size distributions of elements collected in cascade impactor samples that were placed in-stack and downstream from the ESP-equipped units at each plant. The emission factors (ng/J heat input) of several elements are plotted vs. the aerodynamic diameters of particles. Physical diameters were determined by sizing particles on impactor stages and backup filters via SEM and transformed to aerodynamic diameters using the particle density and slip-correction factor (*32*). We corrected the mass of each element present on backup filters by the excess mass resulting from bounce off and reentrainment of large particles as described previously (*22*). Thus, we can estimate more accurately the fraction of each element emitted in submicrometer particles.

Significant amounts of several elements, including V, W, Ga, Mo, Ca, Br, Ba, Se, As, Sb, U, Fe, Cr, Zn, Co, and Mn, were emitted in submicrometer particles. The fraction of other elements in submicrometer particles is generally much less, but too small to determine accurately (*22*).

We attempted to evaluate wall losses by comparing concentrations in impactor and filter samples; because of the variation between successively collected samples, accurate comparisons could not always be made. In general, however, concentrations of elements in the flue gas, which were determined by summing the amounts on impactor stages, were typically from 10 to 60% lower than concentrations on filters in samples from the ESP at plant A and from 12 to 40% lower in samples from the ESP at plant B. The magnitude of the discrepancy depended on the specific element, its distribution among particle sizes, and sampling time (see ref *22*).

Aerosol-Distribution Parameters of Minor and Trace Elements. Elemental mass median aerodynamic diameters (EMMAD) were determined from analyses of cascade impactor samples collected at each of the units and they are listed in Table IV. These data reflect only the larger particle modes. Ranges of median EMMADs of particulate emissions from the plant A and plant B ESP units were 1.8–4.9 and 4.3–12.1 μm, respectively. Thus, as in the case of the total aerosol (see Table III), the EMMADs of particles from the more efficient ESP were smaller.

Elements in emissions from each of the units show distinct behavior in their distributions according to particle size. At plant A, the distributions of Al, Ce, Cl, Fe, Hf, K, La, Na, Sc, and Th were nearly identical. The EMMADs of particles containing As, Ba, Ga, I, U, V, W, and Zn were about half those of particles with elements in the Al group. The EMMADs of Co, Cs, Cu, Mo, Mn, and Sb were slightly smaller than those containing the Al group. If an element were distributed on only the surfaces of aerosol particles, then its mass distribution would coincide with the surface-area distribution of the aerosol. The calculated surface-area median aerodynamic diameters (SMAD) of elements in the Al group (about 1.8 for particles having an EMMAD of 2.5 μm and σ_g of 2.3) are nearly equal to the EMMADs of elements in the As group, thus indicating surface occurrence of elements in the As group on particles containing elements in the Al group. This would occur if these elements were deposited from the vapor phase;



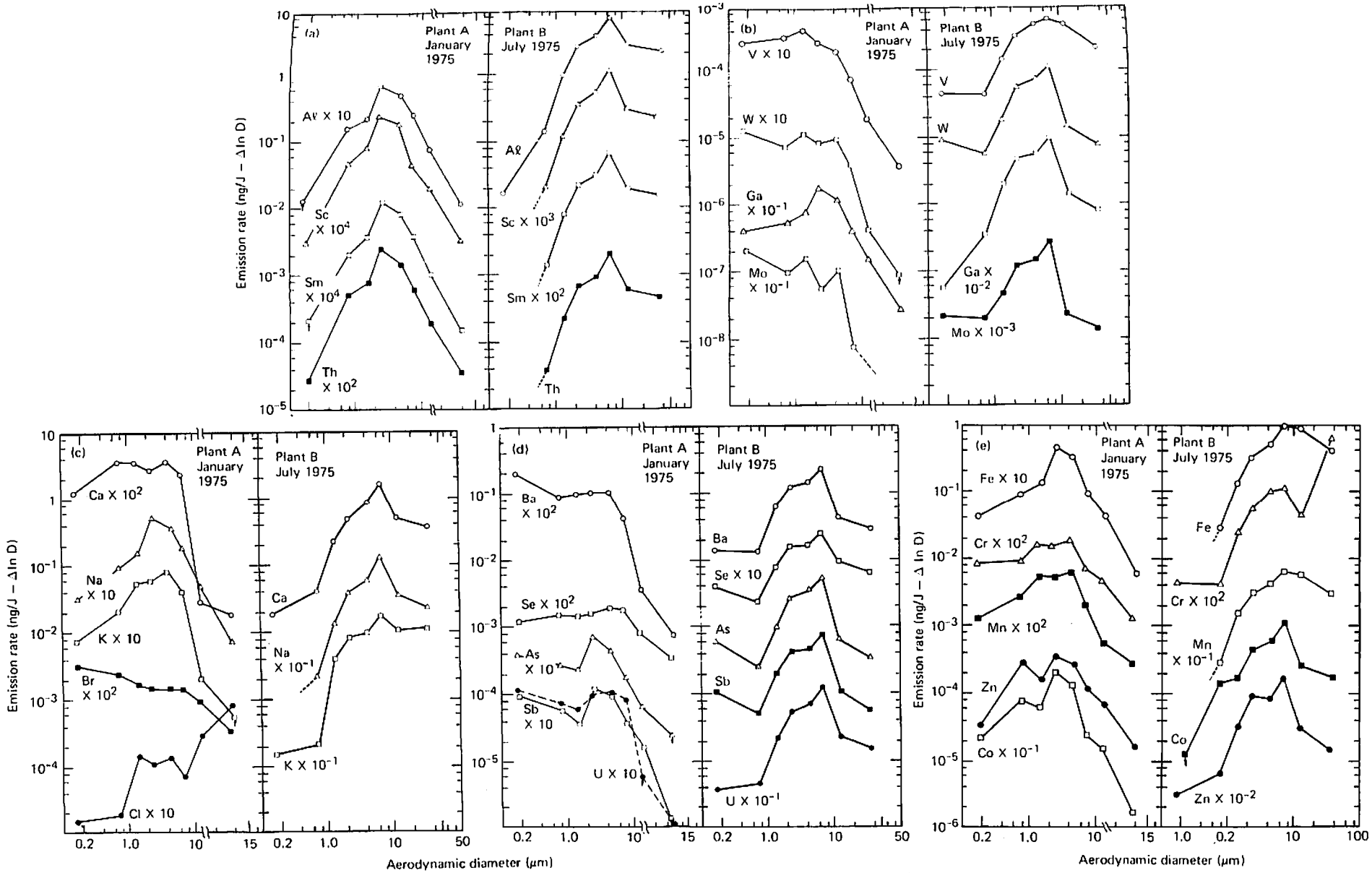


Figure 1. Typical distributions of mass vs. particle size of elements in aerosols emitted from two coal-burning steam-generating units. Masses of elements are expressed as emission rates per joule of heat input to the boiler as discussed in the text

Table IV. Elemental Mass Median Aerodynamic Diameters of Aerosols from Two Coal-Fired Electrical Generating Units, μm

Plant A January 1975			Plant B July 1975		
Elements	EMMAD[a]	σ_g[b]	Elements	EMMAD[c]	σ_g[b]
La, Tb, Sc	~4.5	1.4 - 2.8[d]	Cr, Cs, Rb, Zr	~12	2.2 - 3.0
Sm, Nd, Mg, Lu, Yb, In, Eu	~3.3	1.4 - 2.4 3.0[d]	Al, Br, Ce, Co, Dy, Eu, Fe, Hg, K, La, Lu, Mg, Nd, Sc, Sm, Ta, Tb, Th, Ti	~9.5	2.2 - 3.2
Hf, K, La, Sc, Th, Al, Ce, Cl, Na	~2.5	1.6 - 2.7[d] 1.8 - 2.3			
Ca, Mo, Sb, Cu, Mn, Co, Cs, Rb, Ti, Fe	~2.3	1.5 - 2.6	As, Ba, Ga, In, Mo, Sb, U, V, W, Zn	4.4 - 6.3	1.9 - 3.4
Br, Cr, U, W, Zn, Ga, Sr, I, As, Ba, V	~1.7	1.5 - 2.0 (2.1 - 3.7)[d] 1.5 - 2.3 (2.1 - 4.2)[d] 1.6 - 2.9			

[a] EMMADs estimated from up to five impactor samples. The relative standard deviation of successive determinations of the EMMADs was typically about 20%, but errors among elements are typically ≤10%. [b] Geometric standard deviation. [c] Range of median values of EMMADs of up to six impactor samples for each element. [d] Value corresponds to element underlined.

Table V. Emission Factors of Elements in Particles from Generating Units at Two Coal-Fired Power Plants (pg/J) [a]

	Plant A January 1975 Median	Minimum	Maximum	Plant B ESP Unit July 1975 625-MW Sample[b]	Minimum	Maximum
Al	320 ± 13	286	354	15,600 ± 500	3860	21,700
As	0.22 ± 0.014	0.15	0.22	15.3 ± 0.3	5.77	15.3
Ba	10.8 ± 1.6	10.3	11.1	807 ± 10	243	807
Be	–			0.72 ± 0.24	0.42	0.72 (3)
Br	0.125 ± 0.035	0.091	0.20	6.6 ± 3.5		(1)
Ca	216 ± 35 (2)	188	243	3400 ± 100	1590	3940
Cd	–			0.26 ± 0.04	0.097	0.26 (4)
Ce	0.48 ± 0.02	0.41	0.52	16.0 ± 0.5	8.25	21.3
Cl	0.98 ± 0.42	0.37	1.7	–		
Co	0.10 ± 0.01	0.084	0.11	2.38 ± 0.04	1.12	3.05
Cr	0.81 ± 0.07	0.68	1.0	9.58 ± 0.36	3.1	30.5
Cs	0.042 ± 0.002	0.036	0.068	0.410 ± 0.031	0.209	0.615
Dy	–			1.12 ± 0.03	0.324	1.52
Eu	0.0061 ± 0.0004	0.0047	0.0070	0.164 ± 0.005	0.0847	0.218
Fe	156 ± 7	130	187	3670 ± 40	1980	5350
Ga	0.59 ± 0.18	0.49	0.63	18.7 ± 1.0	9.74	19.8
Hf	–			1.37 ± 0.03	0.717	1.85
I	3.5 ± 0.3	3.2	4.4	–		
In	0.0024 ± 0.00014	0.0023	0.0031	0.108 ± 0.006	0.0339	0.108
K	43 ± 20	26	46	905 ± 200	441	1130
La	0.26 ± 0.014	0.22	0.32	8.96 ± 0.09	4.75	12.0
Lu	0.0032 ± 0.0004 (2)	0.0029	0.0036	0.164 ± 0.007	0.0701	0.231
Mg	–			1360 ± 380	1170	3240
Mo	0.079 ± 0.010	0.057	0.15	6.48 ± 0.76	2.26	8.61
Mn	0.45 ± 0.03	0.42	0.47	41.2 ± 0.5	9.07	41.2
Na	121 ± 5	77	160	2210 ± 10	1120	2810
Nd	0.21 ± 0.06	0.13	0.21	6.05 ± 0.48	3.42	8.40
Rb	0.37 ± 0.12 (1)			5.52 ± 0.57	2.52	7.52
Sb	0.052 ± 0.003	0.048	0.054	2.15 ± 0.04	0.863	2.15
Sc	0.074 ± 0.0014	0.061	0.084	1.96 ± 0.02	1.03	2.72
Se	0.26 ± 0.02	0.14	0.27	5.82 ± 0.16	2.83	6.07
Sm	0.033 ± 0.002	0.029	0.036	1.14 ± 0.06	0.648	1.60
Sr	5.4 ± 0.8 (1)			85.4 ± 8.0	32.2	111
Ta	0.0077 ± 0.0014	0.0056	0.0098	0.323 ± 0.13	0.158	0.441
Tb	0.0042 ± 0.0005 (2)	0.0036	0.0047	0.112 ± 0.006	0.060	0.158
Th	0.082 ± 0.004	0.065	0.091	3.67 ± 0.06	1.96	5.09
Ti	24 ± 8 (2)	17	31	892 ± 90	338	1150
U	0.091 ± 0.014	0.084	0.10	3.29 ± 0.15	1.39	3.29
V	0.99 ± 0.04	0.65	1.8	39.7 ± 3.2	17.3	39.7 (5)
W	0.091 ± 0.009 (1)			2.78 ± 0.18	1.20	2.78
Yb	–			0.503 ± 0.019	0.271	0.789
Zn	1.6 ± 0.14	1.2	1.8	44.8 ± 2.4	16.5	44.8
Zr	1.6 ± 0.7 (1)			34.6 ± 7.1	13.1	41.1

[a] All values are based on analyses of filter samples only and were calculated on a dry gas basis at standard temperature and pressure. The water vapor contents of stack gasses were 9.2 and 7.9% at plants A and B, respectively. The data reflect three and six samples for plants A and B, respectively, or the number in parentheses. Uncertainties reported are analytical uncertainties only; the total uncertainty in any given determination is typically about 20%. [b] Results of a single sample collected when the unit operated at 83% capacity and with four precipitator sections inoperative.

Table VI. Penetration of Elements Contained in Particles through the Boilers and ESPs at Two Coal-Fired Power Plants (%)

Plant A Element	Penetration[a]	Plant B Element	Penetration[b]
Br, Cl	0.029, 0.006	Br	0.24
Al, Ti, Mn, K, Ca, Hf, Ta, Yb	0.07 - 0.13	Al, Sc, Lanthanides (Th, Ti, Ta, Fe, Be, Mg, Ca, Na, K, Rb	0.9 - 1.6
Sm, La, Th, Ce, Fe, Sc, Na, Lu, Sr, Cs	0.14 - 0.24	Mn, Co, Cr	1.6, 2.5, 3.8
V, Cr, Ba, Co	0.29 - 0.40	U, V, Ba, Ga, Mo, Pb, In	3.7 - 5.5
U, Se, Ga	0.53, 0.56, 0.65		
Zn, In, Sb, As	0.78 - 1.1	As, Cd, Se, Sb, W, Zn	6.3 - 11.5

[a] Range of median values of up to six samples. [b] Range of median values of up to eight samples. Penetration is defined as [atmospheric emission factor (ng J^{-1})/input (ng J^{-1})] × 100 (see text).

however, the computation is quite sensitive to the value of the σ_g.

Median EMMADs of rare earths, Al, Fe, Co, Cr, K, Mg, Ti, Zr, and Sc, emitted from the ESP unit at plant B (Table IV) ranged from about 9 to about 12 μm; those containing As, Ba, Ga, In, Mo, Sb, U, V, W, and Zn ranged from about 4 to 6 μm, or about half those containing elements in the Al group and near the SMADs, i.e., 5.1 μm for MMAD of 8.87 μm and σ_g of 2.87, of particles with elements in the Al group. The EMMADs of Ca, Na, Sr, and Se were generally intermediate between those containing the As and Al groups.

On comparing the EMMADs of particles emitted from ESP units at the two plants, elements in the large particle mode from plant A seem to be distributed somewhat more heterogeneously than elements in the corresponding mode from plant B. Rather high EMMADs were often observed for particles containing Br, Cl, and I (4.0, 15, and 3.7 μm, respectively) in aerosol particles from the ESP at plant A, and for Se-containing particles (5.8 μm at plant A and 9.5 μm at plant B) in aerosols from both plants. These elements are the most volatile of the elements detected, and the high EMMADs may result from the adsorption of vapors either by large porous particles or by impactor substrates. In the latter case the data may be in error. Studies to determine the importance of adsorption of vapor-phase elements on impaction substrates are in progress at our laboratory.

Partitioning and Atmospheric Emission of Elements. In Table V we list emission factors (pg/J) of elements in samples from plant A. As noted above, wall and interstage losses were severe in impactor samples collected from these ESP units. Therefore, the emission factors of elements were derived only from filter samples.

For data from plant B, instead of median values, we report values determined from a sample collected while the unit was operated at 625 MW (about 80% load). During all tests, four ESP sections were inoperative; however, the unit was operated in compliance with emission standards by reduction of the gross generating load. By far, the lowest emissions were measured consistently from plant A. Emissions from the Valmont Unit 5 (*9*) and Allen Steam Plant (*11*) (not shown) were generally in the range between those of plants A and plant B.

Further normalization of the data in Table V by dividing by the input rates of the elements in coal (expressed in ng/J) yields the penetration of each element through the boiler and ESP. Penetrations of elements are independent of their concentrations in coal and are listed in Table VI for both of the generating units.

Penetrations varied considerably, as did emissions, with the element and specific power unit. In general, the lowest pene-

trations were observed for lanthanides, Th, Zr, some alkali metals, Sc, and Al, all of which tended to be in particles with the largest MMADs (see Table IV) and are associated largely with fly ash resulting from penetration of residual mineral matter. Elements associated with smaller particles, i.e., those in the As group, typically had the largest penetrations. Penetrations of Br and Cl were quite low relative to other elements. Klein et al. (*11*) and others suggested that significant quantities of some highly volatile elements such as Br, Cl, Se, and Hg have significant gas-phase components. Indeed, a rough mass balance indicates that between 7 and 35% of the Se contained in coal is emitted from plant B in the vapor phase.

Median penetrations of elements in large particles were about 0.2% at plant A and about 1.4% (625-MW sample) at plant B. These values correspond to 99.8 and 98.6%, respectively, for the net removal efficiency of these elements. At both plants, about 20% of the ash is removed from the boiler as bottom ash, and the remaining 80% enters the emission-control systems. Given the efficiency of the ESPs at the two plants (99.7 and 97.5% for the total aerosol), the net efficiencies for the removal of total aerosol of the bottom-ash–ESP systems are 99.8 and 98.5% at plants A and B, respectively. The removal efficiencies of elements and total aerosol agree very closely at both plants. This indicated that only a small portion of the mass of elements is contained in fine particles that have higher penetrations.

Thus, the penetration of elements associated with the large-particle fly-ash mode that is derived from residual mineral matter and termed lithophilic by Klein et al. (*11*) is nearly equal to the penetration of the total aerosol. As noted by Klein et al. (*11*), the penetrations of what appear to be the more mobile elements (classified as calcophiles by Klein et al. (*11*)) that occur in small particles are much higher, their concentrations thereby becoming enriched in the total aerosol relative to the nonmobile matrix elements. The enrichment of elements in the combustion process and in systems for the removal of fly ash may be expressed by the ratio of the penetration of a given element to that of the total aerosol or to that of an element whose penetration is similar to the total aerosol. The ratios of penetrations of each of the elements to that of Sc are listed in Table VII for the two plants and plotted vs. particle diameter in Figure 2. Because of this internal normalization, the penetration ratios are identical with an enrichment factor obtained via double normalization of the concentrations of elements in in-stack fly-ash and coal samples. We will refer to the penetration ratios or enrichment factors as relative penetrations (RP). Relative penetrations are affected by the distribution of the element among particle sizes, vapor–particulate fractionation of the element, and the particle-size collection-efficiency curve of the control system.

Relative Penetration vs. Particle Size. As suggested by Gladney et al. (*12*), the elements may be classified conveniently on the basis of the curves of the relative penetration (or enrichment factor) vs. particle size. At plant A, these curves for the lanthanides, K, Ti, Mg, Cs, Rb, Hf, Ta, Sc, and Mn were similar to that for Th (Figure 2a). These show no change in concentration throughout the size range of particles. Curves for Ce, Na, Sr, and Fe were similar to those of the Th group, but were slightly enriched in the smallest sized particles. The curves for K and Ti are similar to that for Fe, but are displaced below Sc (≡1) in relative penetration. The penetration of Ca (Figure 2a) was less than that of Sc, i.e., RP < 1, in larger particles, but greater in smaller particles.

At plant A, the curves of RP vs. particle size for V, Sb, and As were similar to that of Ba (Figure 2a). The RPs of these elements on small particles were the largest observed. Several elements, including Br, Se, Cr (Figure 2b), Mn, Ta, Co, and

Table VII. Relative Penetration of Elements [a] in Aerosols from Several Coal-Fired Power Plants

	This Work			Other Studies		
	Plant A Average[b]	Plant B 625 MW[c]	Plant B 515–530 MW[d]	Allen[e]	Chalk Point[f]	Valmont[g]
Sb	7.0 ± 2.0	5.3 ± 1.0	4.0 ± 0.7	6.7	4.0	–
Cd	–	6.0 ± 2.1	–	–	–	–
W	–	4.9 ± 3.0	3.7 ± 1.3	–	–	–
As	6.6 ± 1.2	7.9 ± 4.1	5.7 ± 1.0	6	6.3	–
In	5.5 ± 2.2	3.7 ± 1.0	2.6 ± 0.7	–	–	–
Zn	4.3 ± 1.2	4.3 ± 1.1	3.0 ± 0.5	7.8	1.5	2.5
Pb	–	3.8 ± 1.5		8.1	3.7	3.1
Ga	4.3 ± 1.6	3.0 ± 1.0	2.8 ± 0.6	–	1.2	–
U	3.3 ± 0.5	2.5 ± 0.6	1.9 ± 0.15	–	–	–
Se	3.0 ± 1.4	5.3 ± 1.2	4.5 ± 0.7	5.5	5.7	1.7
Ba	2.5 ± 0.6	2.7 ± 1.1	1.8 ± 1.0	0.7	0.92	–
Cr	2.5 ± 0.4	2.6 ± 0.4	1.75 ± 0.26	3.0	1.1	–
Co	2.3 ± 0.2	1.7 ± 0.4	1.5 ± 0.1	1.4	1.0	–
V	2.0 ± 1.5	2.5 ± 0.8	2.2 ± 0.7	2.5	0.75	–
Mo	1.8 ± 1.4	3.5 ± 1.7	2.7 ± 0.9	–	–	3.0
Rb	1.8 ± 0.7	0.89 ± 0.16	0.81 ± 0.09	0.75	–	0.94
Cs	1.7 ± 0.4	0.82 ± 0.28	0.80 ± 0.14	1.5	–	–
Sr	1.2 ± 0.2	1.4 ± 0.4	1.3 ± 0.3	1.0	–	–
Eu	1.2 ± 0.15	0.92 ± 0.12	0.92 ± 0.08	0.79	0.75[h]	–
Mg	1.1 ± 0.2	0.8 ± 0.5	1.5 ± 0.6	0.54	–	–
Fe	1.1 ± 0.1	0.90 ± 0.14	0.94 ± 0.02 (0.05)	0.84	0.83	≡1.0
Ce	1.06 ± 0.07	0.88 ± 0.14	0.86 ± 0.02 (0.05)	–	0.75[h]	–
Na	1.0 ± 0.2	1.1 ± 0.15	1.1 ± 0.2	0.99	1.0	–
Sc	≡1.00 ± 0.13	≡1.00 ± 0.12	≡1.00 ± 0.12	≡1.0	≡1.0	–
Lu	1.0 ± 0.4	0.97 ± 0.14	0.97 ± 0.02	–	0.75[h]	–
La	1.0 ± 0.1	0.88 ± 0.12	0.86 ± 0.06	0.68	0.75[h]	–
Yb	–	0.89 ± 0.16	0.94 ± 0.05	–	0.75[h]	–
Hf	–	0.87 ± 0.12	0.86 ± 0.04	0.76	–	–
Sm	1.0 ± 0.15	0.96 ± 0.29	0.97 ± 0.05	0.55	0.75[h]	–
K	1.0 ± 0.4	0.7 ± 0.3	0.68 ± 0.10	0.95	0.83	–
Tb	0.97 ± 0.19	0.96 ± 0.16	0.93 ± 0.11	–	0.75[h]	–
Ta	0.95 ± 0.27	0.89 ± 0.16	0.88 ± 0.06	1.0	–	–
Th	0.95 ± 0.19	0.90 ± 0.13	0.90 ± 0.03	0.76	–	–
Ti	0.91 ± 0.18	1.0 ± 0.1	0.9 ± 0.3	1.2	0.75	–
Al	0.86 ± 0.07	0.75 ± 0.16	0.73 ± 0.08	0.44	0.83	0.94
Nd	0.84 ± 0.22	0.89 ± 0.28	0.91 ± 0.07	–	0.75[h]	–
Ca	0.76 ± 0.19	0.89 ± 0.28	0.81 ± 0.12	–	0.92	–
Zr	0.7 ± 0.3	0.96 ± 0.42	0.91 ± 0.18	–	0.83	0.73
Mn	0.68 ± 0.17	1.1 ± 0.7	0.85 ± 0.25	0.78	–	–
Be	–	0.6 ± 0.4	–	–	0.64[i]	–
Br	0.2 ± 0.1	0.1 ± 0.1	–	–	0.17	–

[a] Penetration (Table VI) of each element to that of Sc, which is identical with the enrichment factor used by Gladney et al. (*12*) and Gordon et al. (*33*). [b] The uncertainty reported is the larger of twice the standard deviation and twice the analytical uncertainty. Rb is based on one sample. [c] The uncertainty reported is twice the individual uncertainty in the ratio that was derived from standard deviations of replicate elemental analyses of coal and aerosol samples. [d] Uncertainties reported are twice the standard deviation of the replicate determinations; twice the root mean square of the individual uncertainties is given in parentheses if larger than the 2σ value. [e] Based on 1973 data of Klein et al. (*11*). [f] Unless indicated, values listed are based on data of Gladney et al. (*12*). [g] Derived from data of Kaakinen et al. (*9*) for the ESP-equipped unit. Data normalized to Fe. The value for Pb was based on ^{210}Pb. [h] Based on single value reported for "rare earths" in Gordon et al. (*33*). [i] Based on value of Gladney and Owens (*34*) renormalized to Sc.

to a lesser extent Zn, were definitely enriched in larger particles as well as in smaller particles. Gladney et al. (*12*) observed similar enrichments of Se and Hg in large particles. Significant quantities of Se, Hg, and Br are in the vapor phase in flue gasses and may have been adsorbed onto impactor substrates, on large porous particles, or on large carbonaceous particles, which we saw on the upper stages of impactors collected at plant A.

Curves of RP vs. particle size for elements in plant B aerosols are shown in Figure 2c. Curves for the lanthanides, K, Hf, Th, Ti, Mg, Cs, Rb, Ta, Sc, and Mn were similar to those for Na and Fe. These showed little or no enrichment in any sized particle. Enrichments of W, U, Ba, Zn, V, In, Ga, Ba, As, Se, Sb, and Mo are considerable and increase with decreasing particle size. Curves for these elements tended to be somewhat bimodal (see W) with a broad maximum between 2 and 10 μm (see W, U, and Ba in Figure 2b). The curves for Se differ somewhat from those of W, U, and Ba in that the minimum is broader. Both Cr and Co (Figure 2c) were highly enriched in the smallest sized particles, but the curves of RP vs. size were distinctly different from those of elements with curves similar to W.

Relative Penetration of Elements. In column 4 of Table VII we list RPs of elements from five samples collected at plant B when the load was 515 or 530 MW. Despite the rather large range in the absolute elemental emission rates (typically twofold or more, see Table V), the penetration ratios of the

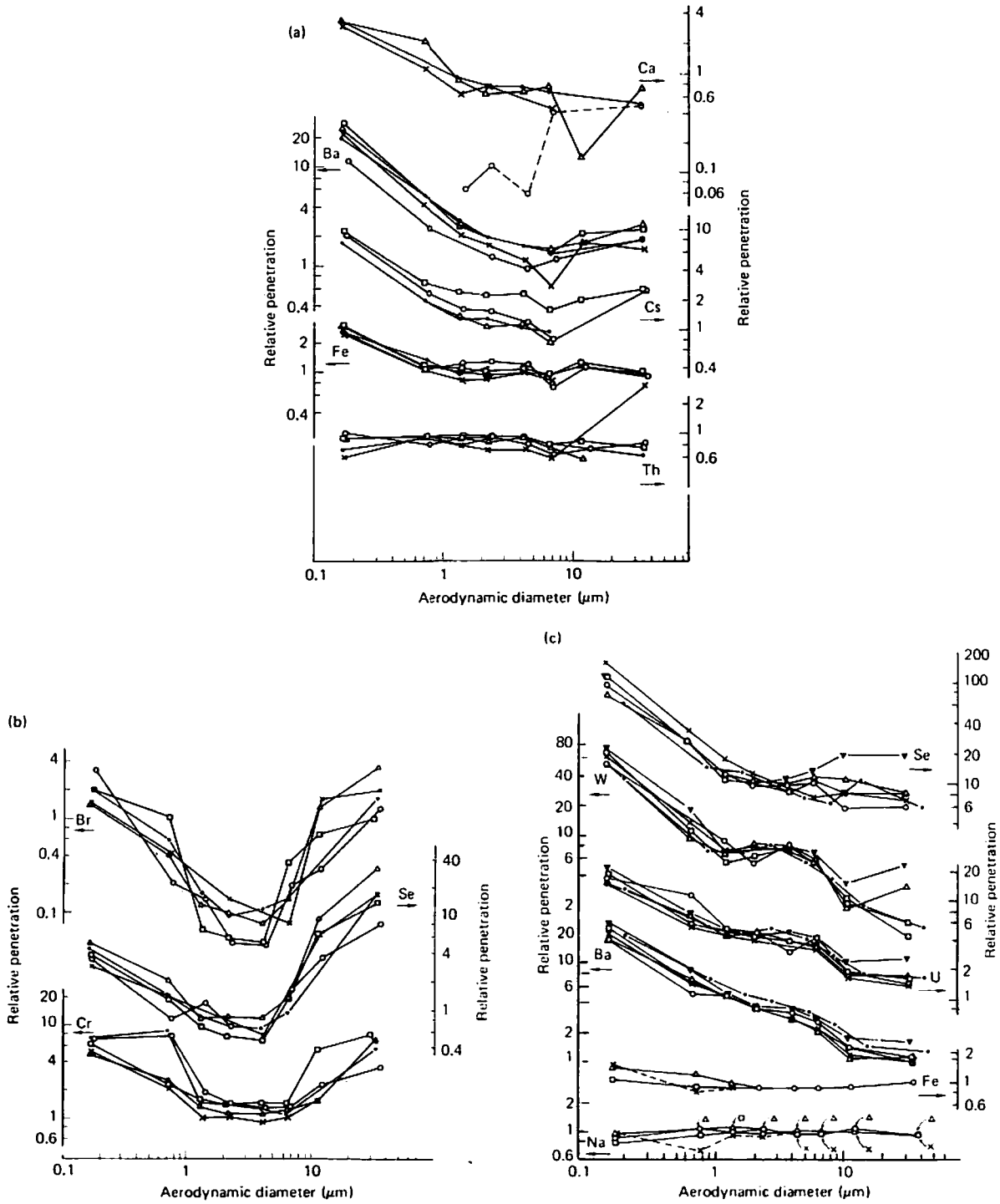


Figure 2. Relationship of relative penetration to particle size of several elements in aerosols emitted at plant A (a and b) and plant B (c). The symbols indicate different sets of data from impactors

515- and 530-MW samples varied by less than the uncertainties in the individual values (2σ typically is <20%). Thus, for a given plant it appears possible to determine the RP of elements on the basis of only a few samples. Further comparison of the penetration ratios of the 625-MW and 515- to 530-MW samples shows significant, but relatively small, differences for a few elements: As, Cr, In, Mo, and Sb. Thus, the penetration ratios of the elements seem to be relatively independent of gross generating load as well as absolute emission rate.

Despite the rather large differences in the composition and origin of the coal and differences in the combustion chambers and ESPs used at the two plants, the RPs of most of the elements were equivalent to within their respective uncertainties. In fact, except for In, Se, Mo, Rb, Cs, K, Mn, and Br, the deviation between the two values (larger/smaller × 100) was ≤35%. The largest differences in the two units were in values of In, Se, Mo, Rb, Cs, K, and Mn. Differences in RPs of the elements ranged from 1.4 for K to about 2 for Rb and Cs. However, only Rb, Cs, Mo, Se, and Mn are judged to be significantly different. The larger penetrations of Rb and Cs at plant A probably result from significantly greater concentrations of these elements in smaller particles as indicated in the curves of RP vs. particle size shown for Cs in Figure 2a. At plant B, the curves of relative penetration vs. particle size for Rb and Cs are similar to those shown for Fe and Na (Figure

2b).

Also listed in Table VII are the RPs of elements determined at three other conventionally designed coal-fired power units equipped with cold-side ESPs. During the work of Gladney et al. (*12*), the plant at Chalk Point burned high-sulfur (1.9%) coal with an ash content of about 12%. The Valmont plant burned low-sulfur (0.6%), low-ash (6%) coal. Coal at the Allen Steam Plant contained 10.4% ash and 3.1% S (1973 data of Klein et al. (*11*)). The removal efficiences for fly ash at the Chalk Point, Valmont, and Allen Steam Plants were estimated at 97, 96.2, and 99.5%, respectively, including bottom-ash removal and other fly-ash-collection systems in addition to ESPs. Despite these differences, many of the values from these units are remarkably similar to those determined at plants A and B. The largest differences in the RPs at the five plants were those of Zn, Pb, Ba, Cr, Co, V, Rb, and Cs, which differed by as much as a factor of five. These include elements in each of the three geochemical classifications (i.e., chalophilic, Zn and Pb; lithophilic, Cs and Rb; and intermediate elements, Ba, Cr, Co, and V) described by Klein et al. (*11*). The large range in RPs of these elements is attributed to differences in distributions of elements according to particle size (and hence coal chemistry) and the removal efficiency vs. particle size curves of the ESPs.

Summary and Conclusions

The relative penetrations of several elements from two western coal-fired power plants are nearly the same, despite variations in boiler size, electrical generating capacity, precipitator size and efficiency, and coal composition, and are quite similar to those observed at plants burning high-sulfur Eastern coal. However, significant differences exist among plants in relative penetrations of the elements Zn, Pb, Ba, Cr, Co, V, Rb, and Cs. This is attributed to differences in composition of the coal and the particle size vs. efficiency characteristics of the individual ESP's. Based on concentrations of elements reported by Gluskoter et al. (*35*), enrichments relative to average crustal abundances in U.S. coals are often larger and more highly variable than enrichments (RPs) that occur during coal use in the power plants discussed above. Thus, excluding fractionation of elements that can occur in power plant plumes (*15*), the greatest impact on the final enrichment of many elements in particles emitted from these plants is due to the original coal composition. We note, however, that enrichments of elements in particles emitted from coal-burning units equipped with other types of particulate control systems such as venturi scrubbers can be much greater than those reported above (*21*).

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Literature Cited

(1) Coles, D. G., Ragaini, R. C., Ondov, J. M., *Environ. Sci. Technol.*, 12, 442 (1978).
(2) Eisenbud, M., Petrow, H. G., *Science*, 144, 228 (1964).
(3) Martin, J. E., Harward, E. D., Oakley, D. T., Smith, J. M., Bedrosian, P. H., in "IAEA Symposium on Environmental Aspects of Nuclear Power Stations, New York, 1969", IAEA Conference 700810-24, paper IAEA-Sm-146/19, 1969, pp 325-37.
(4) Hull, A. P., *Nucl. News*, 51-5 (April 1974).
(5) Moore, H. E., Martell, E. A., Poet, S. E., *Environ. Sci. Technol.*, 10, 586-91 (1976).
(6) Guerrini, R., Pennacchi, A., "La Rivista Dei Combustibili", Vol. XXIX, fasc. 7-8, Luglio-agosto, 1975.
(7) Hangebrauck, R. P., Vonlehmden, D. J., Meeker, J. E., *J. Air Pollut. Control Assoc.*, 14, 267-78 (1964).
(8) Jones, P. W., Giammar, R. D., Strup, P. E., Stanford, T. B., *Environ. Sci. Technol.*, 10, 806-10 (1976).
(9) Kaakinen, J. W., Jorden, R. M., Lawasani, M. H., West, R. E., *Environ. Sci. Technol.*, 9, 862-9 (1975).
(10) Bertine, K. K., Goldberg, E. D., *Science*, 173, 233-5 (1971).
(11) Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talm, Y., Van Hook, R. I., Bolton, N., *Environ. Sci. Technol.*, 9, 973-9 (1975).
(12) Gladney, E. S., Small, J. A., Gordon, G. E., Zoller, W. H., *Atmos. Environ.*, 10, 1071-7 (1976).
(13) Block, C., Dams, R., *Environ. Sci. Technol.*, 10, 1011-7 (1976).
(14) Ragaini, R. C., Ondov, J. M., *J. Radioanal. Chem.*, 37, 679-91 (1977).
(15) Ondov, J. M., Ragaini, R. C., Bierman, A. H., Choquette, C. E., Gordon, G. E., Zoller, W. H., paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, March 25, 1977, Abstract ENVT-124, Lawrence Livermore Laboratory, Preprint UCRL-78825, 1977.
(16) Andren, A. W., Klein, D. H., *Environ. Sci. Technol.*, 9, 856-8 (1975).
(17) Billings, C. E., Matson, W. R., *Science*, 176, 1232-3 (1972).
(18) Davison, R. L., Natusch, D. F. S., Wallace, J. R., Evans, E. A., Jr., *Environ. Sci. Technol.*, 8, 1107-13 (1974).
(19) Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., Jr., Williams, P., *Science*, 191, 852-4 (1976).
(20) Task Group on Lung Dynamics, *Health Phys.*, 12, 173-208 (1966).
(21) Ondov, J. M., Ragaini, R. C., Biermann, A. H., "Elemental Emissions From a Coal-Fired Power Plant: Comparison of a Venturi Wet Scrubber-System with a Cold-Side Electrostatic Precipitator," Lawrence Livermore Laboratory, Preprint UCRL-80110.
(22) Ondov, J. M., Ragaini, R. C., Biermann, A. H., *Atmos. Environ.*, 12, 1175 (1978).
(23) Ragaini, R. C., Heft, R. E., Garvis, D., "Neutron Activation Analysis at the Livermore Pool-Type Reactor for the Environmental Research Program", Lawrence Livermore Laboratory Report, UCRL-52092, 1976.
(24) Heft, R. E., paper presented at the Third International Conference on Nuclear Methods in Environmental and Energy Research, Columbia, Mo., Oct 10-13, 1977.
(25) Murphy, J., *At. Absorpt. Newsl.*, 14, 151 (1975).
(26) Bonner, N. A., Bazan, F., Camp, D. C., *Chem. Instrum.*, 6, 1-36 (1975).
(27) Ondov, J. M., Zoller, W. H., Olmez, K., Aras, N. K., Gordon, G. E., Ranticelli, L. A., Able, K. H., Filby, R. H., Shah, K. R., Ragaini, R. C., *Anal. Chem.*, 47, 1102-9 (1975).
(28) Ondov, J. M., Ragaini, R. C., Heft, R. E., Fisher, G. L., Silberman, D., Prentice, B. A., in Proceedings of the 8th Materials Research Symposium, Methods and Standards for Environmental Measurement, Gaithersburg, Md., Sept 20-24, in press; Lawrence Livermore Laboratory, Preprint UCRL-78194, 1976.
(29) Fisher, G. L., Chang, P. V., Brummer, M., *Science*, 192, 555-6 (1976).
(30) Ulrich, G. D., "An Investigation of the Mechanism of Fly-Ash Formation in Coal-Fired Utility Boilers", Interim Report, US-ERDA FE-2205-1, May 28, 1976.
(31) Padia, A. S., Sarafim, A. I., Howard, J. B., paper presented at the Combustion Institute's Central States Section, April 1976.
(32) Fuch, N. A., "The Mechanics of Aerosols", MacMillan, New York, 1964, pp 21-30.
(33) Gordon, G. E., Zoller, W. H., Gladney, E. S., Proceedings of 2nd International Conference on Nuclear Methods and Environmental Research, Columbia, Mo., 1974, pp 344-53.
(34) Gladney, E. S., Owens, J. W., *J. Environ. Health*, A11(4&5), 297-311 (1976).
(35) Gluskoter, H. J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B., Kuhn, J. K., "Trace Elements in Coal: Occurrence and Distribution", Illinois State Geological Survey, Circular 499, 1977.

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EX 3

TECHNICAL PAPER

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Comparison of Particle Size Distributions and Elemental Partitioning from the Combustion of Pulverized Coal and Residual Fuel Oil

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ABSTRACT

U.S. Environmental Protection Agency (EPA) research examining the characteristics of primary PM generated by the combustion of fossil fuels is being conducted in efforts to help determine mechanisms controlling associated adverse health effects. Transition metals are of particular interest, due to the results of studies that have shown cardiopulmonary damage associated with exposure to these elements and their presence in coal and residual fuel oils. Further, elemental speciation may influence this toxicity, as some species are significantly more water-soluble, and potentially more bio-available, than others. This paper presents results of experimental efforts in which three coals and a residual fuel oil were combusted in three different systems simulating process and utility boilers. Particle size distributions (PSDs) were determined using atmospheric and low-pressure impaction as well as electrical mobility, time-of-flight, and light-scattering techniques. Size-classified PM samples from this study are also being utilized by colleagues for animal instillation experiments.

Experimental results on the mass and compositions of particles between 0.03 and >20 μm in aerodynamic diameter show that PM from the combustion of these fuels produces distinctive bimodal and trimodal PSDs, with a fine mode dominated by vaporization, nucleation, and growth processes. Depending on the fuel and combustion equipment, the coarse mode is composed primarily of unburned carbon char and associated inherent trace elements (fuel oil) and fragments of inorganic (largely calcium-alumino-silicate) fly ash including trace elements (coal). The three coals also produced a central mode between 0.8- and 2.0-μm aerodynamic diameter. However, the origins of these particles are less clear because vapor-to-particle growth processes are unlikely to produce particles this large.

Possible mechanisms include the liberation of micron-scale mineral inclusions during char fragmentation and burnout and indicates that refractory transition metals can contribute to PM <2.5 μm without passing through a vapor phase. When burned most efficiently, the residual fuel oil produces a PSD composed almost exclusively of an ultrafine mode (~0.1 μm). The transition metals associated with these emissions are composed of water-soluble metal sulfates. In contrast, the transition metals associated with coal combustion are not significantly enriched in PM <2.5 μm and are significantly less soluble, likely because of their association with the mineral constituents. These results may have implications regarding health effects associated with exposure to these particles.

IMPLICATIONS

Transition metals are hypothesized to play a significant role in causing adverse health effects associated with exposure to $PM_{2.5}$. The concentration, speciation, and solubility of transition metals in $PM_{2.5}$ generated by the combustion of fossil fuels can depend upon the fuel type and combustor design. The results presented in this paper have implications for policymakers and researchers evaluating possible sources and control of $PM_{2.5}$ containing transition metals.

INTRODUCTION

Fine PM has been of considerable environmental interest in recent years because of a number of research studies correlating short-term exposure of ambient levels of fine PM with acute adverse health effects.[1] These studies were summarized by the U.S. Environmental Protection Agency (EPA)[2,3] and reviewed by EPA's Clean Air Scientific Advisory Committee, which concluded that there was evidence

linking ambient fine PM concentrations and adverse health effects.[4] These studies were the basis for a revision of the National Ambient Air Quality Standards for PM that included a standard for PM <2.5 μm in diameter ($PM_{2.5}$).[5]

In the ambient atmosphere, fine PM is composed primarily of sulfates, nitrates, condensed organics, carbonaceous soot, and inorganic aerosols, formed during high-temperature processes such as the combustion of fuels containing trace quantities of metals and other impurities.[2,6,7] Formation of these small particles is heavily influenced by vaporization, condensation, and other gas-to-particle conversion processes. In contrast, the coarse fraction of PM tends to be composed of particles formed by mechanical (e.g., fragmentation, grinding, crushing, and entrainment) processes. Because they are formed by different mechanisms, the fine and coarse fractions of PM tend to have different compositions. Particle composition has been identified as one of the possible factors driving the adverse health effects associated with exposure to ambient PM.[8]

Health effect researchers have identified at least two aspects of particle composition that appear to exacerbate health damage from particles. The first is related to water-soluble transition metals such as Cu, Fe, Ni, V, and Zn present in the particles.[9–11] The second is aerosol acidity in general. In addition to these composition-related properties, ultrafine particles (those particles <0.1 μm in diameter), regardless of composition, have been identified as potential factors influencing mechanisms for these health impacts.[2] Particles with all of these characteristics (transition metals, acidity, and ultrafine size) are contained in the PM generated from the combustion of fossil fuels such as residual fuel oils and coals. Hence, one might hypothesize fossil-fuel-fired systems to be candidate sources of toxic fine particles that play a significant role in the demonstrated association of adverse health effects with ambient concentrations of fine PM.

The research by Dreher et al.[9–11] has indicated that residual oil fly ash (ROFA) possesses toxic qualities. Unfortunately, the hypothesis that residual oil combustion is the prime source of fine particles causing respiratory distress is not consistent with the currently available epidemiologic data. Residual fuel oils are used in significant quantities in only selected regions of the country. Discounting sales of Bunker C oil, the majority of which is likely to be burned by ships well away from continental coastlines, significant residual oil usage occurs primarily in the northeast and southeast regions of the United States.[12] However, adverse health effects associated with exposure to fine PM are not limited to these regions,[13] suggesting that sources of fine PM other than (or in addition to) those related to residual fuel oil combustion must also be important.

Another source of $PM_{2.5}$ containing transition metals is pulverized coal combustion. Pulverized coal combustion is widespread throughout the United States, and emissions from coal-fired boilers and furnaces account for a much larger fraction of both PM <10 μm in aerodynamic diameter (PM_{10}) and $PM_{2.5}$, compared to residual fuel oil combustion. In 1997, ~165,000 tons of $PM_{2.5}$ was emitted from utility, industrial, commercial, and institutional combustion of coal, compared to 35,000 tons of $PM_{2.5}$ from combustion of residual oil from the same source categories.[14] These values are for primary PM emitted directly from these sources and do not include secondary particles formed from gas-phase precursors such as SO_2 and NO_x. Because both coal and residual fuel oil burned in the United States contain significant levels of transition metals (see Table 1), substantial quantities of these metals are emitted into the atmosphere. In light of the potential health effects associated with inhalation exposure to transition metals, it is worthwhile to explore the formation mechanisms and partitioning of transition metals across different particle sizes for both coals and residual fuel oils.

In a previous study, Miller et al.[15] explored the relationship between residual fuel oil composition, boiler operation, and the physical and chemical characteristics of the PM produced. In a subsequent study, Linak et al.[16] compared the characteristics of PM produced from two types of combustion systems burning the same residual fuel oil. These systems were designed to simulate the operation of small institutional and industrial boilers and large utility boilers. In this study, we compare differences in compositions and particle size distributions (PSDs) of PM from residual fuel oil and coal. Specifically, these tests, conducted at EPA's National Risk Management Research Laboratory in Research Triangle Park, NC, examined the physical and chemical characteristics of PM generated by the combustion of residual fuel oil and coal. A single residual fuel oil was tested in two combustors with significantly different heat transfer characteristics, and three U.S. coals were tested in a single combustor under similar combustion conditions. The purpose of these tests was to examine the relationship between particle size and particle composition, specifically with respect to metal content, for different fossil fuels, and how the relationship may change as fuel or carbon burnout changes. The results of the current and previous studies are intended to form the foundation that may ultimately link measures of acute pulmonary damage to engineering variables.

EXPERIMENTAL

Residual oil experiments were performed in two types of combustion systems. These systems represent extremes of a range of practical conditions under which fuel oil is burned. Although they may not represent specific boilers

Table 1. Fuel analysis.

	Western Kentucky Bituminous	Montana Subbituminous	Utah Bituminous	High Sulfur No. 6 Oil
Proximate Analysis[a] (%)				
Moisture	6.97	11.36	5.97	0.50
Volatile matter	35.86	37.18	38.58	
Fixed carbon	49.66	41.05	45.75	
Ash	7.51	10.41	9.69	0.10
HHV[b], Btu/lb	11291	9526	11289	18270
HHV, kcal/kg	6273	5292	6272	10150
Ultimate Analysis[c] (%)				
C	70.17	64.87	69.23	85.61
H	4.57	3.97	4.87	10.38
N	1.49	1.03	1.45	0.35
S	3.11	0.83	0.96	2.33
O[d]	12.59	17.56	13.18	0.92
Ash	8.07	11.74	10.31	0.10
Trace Elements[c] (μg/g fuel)				
As	4.68	1	2	0.1
Be	1.6	0.4	0.8	<0.3
Cd	<0.2	<0.2	<0.2	0.60
Cl	35.5	28.7	33.9	
Cr	11	4	12	1.05
Cu	3	2.89	3.37	3.5
Fe	9210	2560	2000	21
Pb	3.06	3.42	2.87	4.5
Mg	79.4	1700	1710	
Mn	6.71	62.3	59.9	
Hg	0.15	0.08	0.07	0.10
Mo	3.25	ND	ND	
Ni	6.35	2.39	ND	30
K	81.7	ND	44.6	
Se	2	1	2	<0.1
Na	332	300	409	
V	13	4.55	4.25	220
Zn	30.8	ND	ND	74

Notes: [a]As received (wet); [b]Higher heating value; [c]Dry basis, ND indicates nondetect analysis, empty cells indicate no analysis for this element was attempted; [d]By difference.

in all respects, they were investigated here with a view to determining how this range of combustion conditions influences the characteristics of fine particles and the mechanisms that form them. The first system is a small fire-tube boiler, in which combustion occurs in tubes surrounded by water or steam. These types of small boilers have large heat transfer surfaces, small volumes, relatively short residence times, cold walls, and high gas quenching rates (~500 K/s), and often produce emissions with relatively high carbon contents due to unburned carbonaceous char. The second system is a laboratory-scale refractory-lined combustor designed to simulate the time/temperature environments of larger utility boilers and incinerators. In large utility boilers, the water or steam, rather than the combustion gases, is contained in tubes. These systems, including the refractory-lined combustor, operate at higher temperatures with lower quenching rates (~150 K/sec). As will be discussed later, particle emissions from this system contain very little unburned carbon and better approximate emissions from large oil-fired utility boilers, as reported in the literature.[17,18]

Fire-Tube Boiler

Residual oil experiments were performed using a commercially available, North American, three-pass, fire-tube package boiler. This unit is equipped with a 732-kW North American burner with an air-atomizing oil nozzle. Oil temperature and oil and atomizing air pressures are independently controlled to ensure proper oil atomization. PM samples were extracted at stack locations at temperatures ranging from 450 to 550 K. Additional system details are presented elsewhere.[15]

Refractory-Lined Combustor

Residual oil experiments were also performed using a 59-kW laboratory-scale refractory-lined combustor. This unit is equipped with an International Flame Research Foundation (IFRF) moveable-block variable-air swirl burner, which incorporates an air-atomizing oil nozzle positioned along its center axis and swirling air, which passes through the annulus around the fuel injector to promote flame stability. The burner was configured for a high swirl flame (IFRF Type 2, swirl no. = 1.48) with internal recirculation. Gas and aerosol samples were taken from stack locations at temperatures of ~670 K. All oil experiments (fire-tube boiler and refractory-lined combustor) were performed at a stoichiometric ratio (SR) of 1.2 without secondary air preheat. Additional system details are presented elsewhere.[16]

Pulverized Coal Combustor

Coal combustion experiments were conducted using a down-fired, refractory-lined furnace rated at 50 kW. A schematic of this furnace is presented in Figure 1. In this combustor, pulverized coal is metered from a screw feeder and carried by transport air through a fuel injector into the combustor. Additional axial and tangential airstreams are metered separately into the variable swirl burner and introduced into the combustor as an annular flow around the coal. These flows can be adjusted to create stable flames with the desired degree of swirl. The vertical 4.1 m downfired combustor is 20-cm inside diameter (ID). At the bottom of the vertical section, the combustion gases make a 90° turn into a 3.7-m-long, 15-cm-ID horizontal sampling

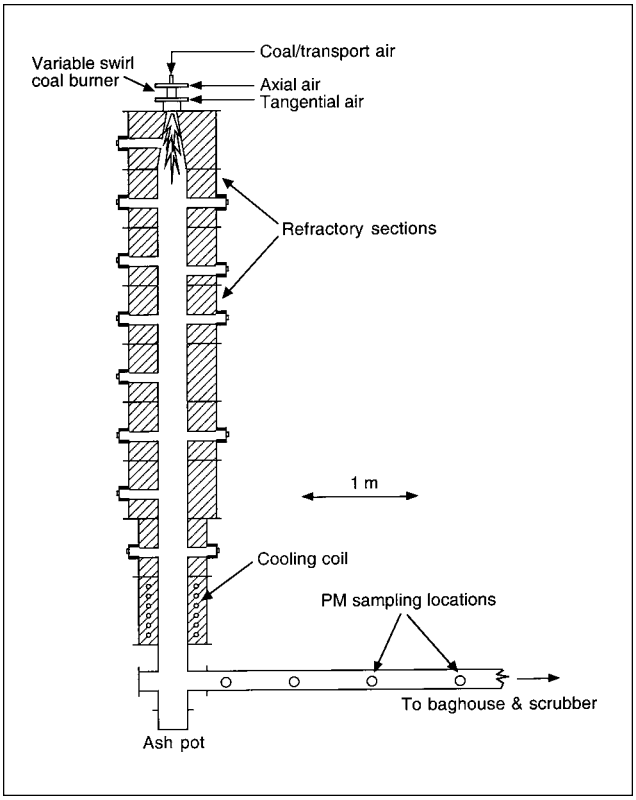

Figure 1. EPA down-fired pulverized coal combustor.

duct. Ports are available along the furnace and exhaust duct for introduction of additional staging air or for introduction of sorbents or extractive sampling. The locations of these ports are shown in Figure 1. Previous test programs burning pulverized coal have resulted in combustion conditions within the furnace similar to those found in full-scale utility units.[19]

Particulate Sampling and Analysis

PM measurements were performed using several methods. Standard EPA Methods 5 and 60 sampling and analytical procedures were used to determine total particulate and metal concentrations using inductively coupled argon plasma atomic emissions spectroscopy (ICP/AES).[20–22] Other metal analyses were determined by X-ray fluorescence (XRF) spectroscopy. Additional samples were analyzed by X-ray absorption fine structure (XAFS) spectroscopy, an element-specific structural analysis that is useful for determining trace element speciation and forms of occurrence in chemically and structurally complex materials such as combustion ash.[23–25]

PSDs were determined by a combination of four techniques used at various times. Instruments based on electrical mobility, time-of-flight, and inertial impaction measurements were used for extracted aerosols; and light-scattering measurements were used for in situ in-stack measurements. Extractive samples were taken for electrical mobility, time-of-flight, and inertial impaction analyses using an isokinetic aerosol sampling system described elsewhere.[26,27] These diluted samples were directed to a TSI Inc. scanning mobility particle sizer (SMPS) and a TSI Inc. aerodynamic particle sizer (APS). The SMPS and APS were configured to yield 54 and 50 channels evenly spaced (logarithmically) over 0.01- to 1.0-µm and 0.5- to 20-µm diameter ranges, respectively. Extracted samples were also directed to three cascade impactors including an Andersen Inc. eight-stage, 28 L/min atmospheric pressure impactor, an MSP Inc. ten-stage, 30 L/min micro-orifice uniform deposit impactor (MOUDI), and a custom-made eleven-stage 28 L/min Berner-type low-pressure impactor.[28] During the oil experiments, in situ light-scattering PSDs were obtained using an Insitec Inc. particle counter sizer velocimeter with a working range of ~0.3–100 µm. Scanning electron microscope (SEM) samples were collected on silver membrane filters to minimize particle charging effects.

In order to collect larger quantities of size-segregated PM for parallel toxicological studies and XAFS analyses, a large dilution sampler capable of sampling 0.28 m^3/min of flue gas was used.[29] The extracted sample passed through a cyclone (50 and 90% collection efficiencies for 1.8- and 2.5-µm-diameter PM, respectively) and was then diluted with clean filtered ambient air (2.8 m^3/min) to approximately ambient temperature (3 sec residence time). The resulting PM was collected on 64.8-cm-diameter Teflon-coated glass fiber filters, transferred to sampling jars, and made available for subsequent chemical, physical, or biological analysis. In addition to the particle sampling and collection devices just described, continuous emission monitors were used to measure stack concentrations of CO, CO_2, NO_x, O_2, and SO_2. These measurements were made in order to monitor and control the combustion environments.

Fly ash samples from the oil experiments and the three coals were subjected to a successive leaching procedure under development to examine the relative solubility of transition metals (Cu, Fe, Ni, V, and Zn) associated with different fly ash matrices. To date, only the dilution sampler filter catches ($PM_{2.5}$) for these four fuels have been examined in this manner. PM samples were placed in successive solutions (30 mL) of distilled water (pH = 7), 0.1 N (equivalent) H_3BO_3 (pH = 5.2 for 0.1 N), 0.1 N CH_3COOH (pH = 2.9), and 0.1 N HCl (pH = 1.1), and sonicated at room temperature for 2 hr. The filtrates and solid residues were separated between successive leaching steps. Finally, these leached samples (and a set of unleached samples) were subjected to a modified Method 3050B extraction procedure to determine total metal content.[30] Briefly, this method uses a 50/50 mixture of HNO_3 and HF, microwaved for 5 min at 340 kPa and 20 min at 550 kPa. After cooling, an additional H_3BO_3 solution is added and

microwaved for 10 min at 340 kPa. Solutes were analyzed by ICP/AES.

Experimental Conditions

The no. 6 residual oil used in both oil experimental systems contained 2.33% sulfur and 0.1% ash. Operational characteristics for both systems included similar oil temperatures (380–400 K), atomizing air pressures (200–240 kPa), and stoichiometries (SR = 1.2). The droplet PSD produced using the Delavan Airo Combustion air-atomizing oil nozzle (model 30615-84) in the fire-tube boiler was relatively narrow with a mean diameter between 30 and 40 μm. The refractory-lined combustor experiments used a similar Spraying Systems Co. (model Air Atom 1/4-JSS) air-atomizing oil nozzle and produced PSDs believed to be similar to those for the boiler studies. Therefore, any differences in carbon burnout may be attributed to differences in temperature history rather than in droplet size. Stack O_2 concentrations ranged between 3.4 and 3.6% for all experiments.

Two western U.S. coals (Montana subbituminous and Utah bituminous) and one eastern U.S. coal (western Kentucky bituminous) have been examined. The coals were burned under conditions that simulated as closely as possible those conditions typical of a full-scale utility boiler. Stack O_2 concentrations for the coal combustion tests ranged from 3.5 to 3.8%, with CO values near 60 ppm for the Montana coal and 135 ppm for the western Kentucky and Utah coals. Heat input rates averaged 22.9 kW for the Montana coal, 19.7 kW for the western Kentucky coal, and 20.2 kW for the Utah coal. Average NO_x concentrations for the three coals ranged between 440 and 480 ppm, and SO_2 concentrations averaged 430 ppm for the Montana coal, 1475 ppm for the western Kentucky coal, and 850 ppm for the Utah coal (all values uncorrected for O_2 concentration).

Table 1 presents the proximate, ultimate, and trace element analyses for the three coals and one residual fuel oil examined. Heating values are also included. In contrast to the residual oil, which contained only 0.1% ash, the coal ash contents ranged from 7.5 to 10.4% (as received). However, the residual oil sulfur concentration was almost as high as the western Kentucky coal (2.33 and 3.11%, respectively). The two western coals each had sulfur concentrations less than 1%. Also of note are the high transition metal (Fe, Ni, V, and Zn) concentrations in the residual oil and the high Fe concentrations in the coals. Although not measured and presented here, coals often contain very high concentrations of Al, Ca, and Si. Hardesty and Pohl[31] report ranges of Al, Ca, and Si concentrations in U.S. coals of 0.3–2.3, 0.005–1.2, and 0.5–41%, respectively. Galbreath et al.[24] report Al and Si concentrations in a similar high sulfur no. 6 oil of 19 and 94 ppm, respectively. Walsh et al.[32] report ranges of Al, Ca, and Si concentrations from three medium sulfur residual oils of 21–44, 13–23, and 23–89 ppm, respectively.

RESULTS AND DISCUSSION

PM and Trace Element Emissions

PM mass emissions, emission factors, and trace element emissions for the three coals and two fuel oil conditions are presented in Table 2. Also presented are the mass fractions of $PM_{2.5}$, as well as the weight percent of unburned carbon and loss on ignition (LOI). PM emissions for the three coals and one of the two fuel oil conditions are based on triplicate averages. Standard deviations are included. These data indicate that uncontrolled PM emissions from the three coals ranged between 3800 and 4400 mg/m^3 compared to 90 and 180 mg/m^3 for the fuel oil.

Differences seen between the two fuel oil conditions are likely the result of differences in the heat transfer, time/temperature profiles, and quenching rates characteristic of the two types of combustion equipment used, and are consistent with data published from field measurements.[16] However, even though the uncontrolled PM emissions for the three coals are over 20 times greater than those for the oil experiments, Table 2 indicates that the mass fraction of $PM_{2.5}$ for the coals is very much smaller (4.3–6.7%) compared with the oil (40–100%). This is likely due to differences in the chemical and physical nature in which inorganic elements are bound within the two types of fossil fuels. Unburned carbon and LOI values for the two bituminous coals (western Kentucky and Utah) were ~10–11 and 13–14%, respectively. While somewhat high, these values are reasonable for small research coal combustors and not too unusual even for full-scale utility boilers. Lower unburned carbon (0.5%) and LOI (2.3%) are seen for the Montana subbituminous coal and are characteristic of the behavior of lower rank coals. LOI values for the two oil conditions are very different (90 and 0%), and this behavior, again, is likely the result of differences in the heat transfer characteristics between the fire-tube boiler and refractory-lined combustor. Table 2 also indicates that, in general, coal has significantly higher trace element emissions compared with oil (uncontrolled). However, notable exceptions exist, including emissions of V, Zn, and Ni, which are 8–24 times higher from residual oil combustion compared with coal combustion.

Table 3 presents size-classified trace element concentrations as well as weight percents of unburned carbon and LOI in PM less than and greater than ~2.5 μm aerodynamic diameter. These analyses were made from the cyclone and filter catches from the dilution sampling system used to collect large quantities of PM. The data indicate that the fine PM fraction tends to be enriched in many of these trace elements compared with the coarse PM fraction, and

Table 2. PM and trace element emissions and emission rates.[a]

	Western Kentucky	Montana	Utah	High Sulfur No. 6 Oil Fire-Tube Boiler	High Sulfur No. 6 Oil Refractory-Lined Combustor
Total Emissions					
PM emissions[b] (mg/m^3) standard dev.	3807 (564)	4374 (246)	4323 (374)	184 (6)	93
PM mass fraction[c] <2.5 μm	0.043	0.050	0.067	0.395	~1
PM emission factor ($lb/10^6$ Btu) ($kg/10^6$ J)	3.00 1.44e-3	3.30 1.58e-3	3.32 1.59e-3	0.123 5.29e-5	0.052 2.50e-5
Unburned carbon[d] (wt %)	10.2	0.5	10.9		
LOI[4] (wt %)	12.9	2.3	14.5	89.9	~0
Trace Element Emissions (mg/m^3)					
Sb	0.41	0.05		0.0077	
As	0.76	0.41	0.24	0.0063	
Be	0.08	0.03		0.00009	
Cd	0.04	0.01	0.003	0.0035	
Cr	0.57	0.26	0.35	0.011	
Cu	0.33	0.40	0.30	0.170	0.200
Fe	504.75	84.87	92.98	0.740	1.200
Pb	0.11	0.27	0.06	0.089	
Mg	5.83	46.52		1.200	1.700
Mn	0.46	5.23		0.016	
Hg				<0.0022	
Ni	0.48	0.17	0.21	1.200	1.400
Na					2.100
V	1.62	0.48	0.58	9.800	12.000
Zn	2.61	0.30	0.54	3.300	3.000

Notes: [a]Dry basis, concentrations corrected to standard conditions (1 atm, 293 K); [b]PM emissions for four of the five experimental conditions are based on the average of three replicate measurements, standard deviation in parentheses; [c]Based on average mass loadings determined by cascade impactors; [d]Total PM unburned carbon and LOI values are based on the sum of weighted values determined from the dilution sampler filter and cyclone catches (see Table 3).

this enrichment seems to be more pronounced for the oil combustion experiments. In fact, it is noted that essentially all the PM for the refractory-lined combustor oil experiments was <2.5 μm in aerodynamic diameter.

Table 2 presents a comparison of the trace element emissions for the fire-tube boiler and refractory-lined combustor oil experiments. As expected, these concentrations are similar because both systems fired the same high sulfur no. 6 fuel oil. However, in contrast to the PM from the boiler, which exhibited high values for LOI ranging from 60 to 85%, blank-corrected results of filter samples from the combustor tests indicate no mass lost on ignition. The sum of the concentrations of the seven analyzed elements listed in Table 2 for the refractory-lined combustor experiments (last column) account for 21.6 mg/m^3 or ~23% of the total mass emissions. However, if these elements are assumed to exist as sulfates, they then account for 67.1 mg/m^3 or ~72% of the total mass emissions. In fact, XAFS spectroscopy indicated that, while a large portion (40–60%) of the sulfur measured in the fire-tube boiler PM existed as unoxidized organic sulfur (predominantly thiophenic sulfur), essentially all (99%) of the particulate-bound sulfur in the refractory-lined combustor samples was in the form of sulfates.

Emission Factors

The measured mass concentration of 93 mg/m^3 determined from the refractory-lined combustor oil experiments can be converted into an emission factor of ~10.5 $lb/10^3$ gal. This value is comparable to the emission factor of 9.2 $lb/10^3$ gal for no. 6 residual oil-fired boilers larger than 100×10^6 Btu/hr published in AP-42.[33] This comparison lends further support to the hypothesis that the refractory-lined combustor adequately simulates the combustion environment of larger industrial and utility boilers. As reported by Miller et al.,[15] the range of emission factors determined for the fire-tube boiler was approximately twice that for oil-fired utility boilers. However, dilution samples for these experiments indicate that only 30–50% of the PM mass emissions had an aerodynamic diameter <2.5 μm. Hence, the fine PM emission factor for utility boilers may well be greater than that of fire-tube boilers.

Emissions results from this study can be compared to values from the literature. Goldstein and Siegmund[34,35]

Table 3. Trace element concentrations in emitted PM size fractions.[a,b]

	Western Kentucky		Montana		Utah		High Sulfur No. 6 Oil Fire-Tube Boiler		High Sulfur No. 6 Oil Refractory-Lined Combustor	
Trace Element Concentration in Ash Fraction (μg/g)	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**
Sb							48.6	8.20		
As	132	68.4	62.7	45.3	89.0	59.6	35.9	8.60		
Be							0.46	0.15		
Cd	8.7	3.3	<1.0	<1.0	<1.0	<1.0	19.3	1.84		
Cr	132	108	17.5	19.6	110	78.7	60.2	41.3		
Cu	73.5	51.9	96.7	55.6	95.8	51.5	1050	222	2346	0[c]
Fe	76500	88300	4000	3810	16000	14400	3850	2300	13993	0
Pb	34.5	16.1	93.2	48.4	40.2	<12.3	990	94.2		
Mg							6190	2220	19989	0
Mn							73.2	42.8		
Ni	110	86.2	41.5	29.3	109	39.4	8020	2270	16518	0
S (wt %)	1.12	0.46	0.74	0.01	0.68	0.27			3.2	0
V	356	330	111	84.9	186	123	58900	19900	135718	0
Zn	548	265	141	31.9	144	40.3	21000	2740	34245	0
Unburned carbon (wt %)	11.25	8.83	0.43	0.53	12.86	9.89				
LOI (wt %)	14.96	9.96	1.69	2.79	15.68	13.98	86.6	96.9	~0	0

Notes: [a]Dry basis, empty cells indicate no analysis for this element was attempted; [b]<2.5- and >2.5-μm concentrations are determined from size-classified fly ash from the dilution sampler filter and cyclone catches, respectively; [c]No material was recovered from the cyclone catch for this condition, <2.5-μm elemental concentrations were determined from M-29 samples.

examined the effect of fuel type and combustion modifications on PM emissions from a small 37-kW (50-hp) fire-tube boiler. They report similar PM emissions of ~180 mg/m^3 with carbon contents of up to 80% while burning a similar 2.2% sulfur no. 6 fuel oil. They also noted that efforts to increase PM burnout shift the PSD toward the submicron range. Conversely, Cheng et al.[17] and Bacci et al.[18] examined PM emissions from 30-MW (1×10^8 Btu/hr) and 320-MW (1×10^9 Btu/hr) fuel-oil-fired power plants, respectively. PM emissions from these units were reported to be 87 mg/m^3 and 40–50 mg/m^3, respectively, even though the 30-MW unit was equipped with a multicyclone PM control system.

The uncontrolled measured mass concentrations for the three coals can be converted to emission factors ranging from 1.4×10^{-3} to 1.6×10^{-3} kg/10^6 J (3.0–3.3 lb/10^6 Btu). Like the oil experiments, these values are also comparable to emission factors determined for these coals. AP-42[33] estimates that filterable PM emission factors for these pulverized coals from dry-bottom wall-fired and dry-bottom tangentially fired utility boilers would range from 3.3 to 5.5 lb/10^6 Btu. This agreement is remarkable considering the difference in the scales of these units. It is important to note, however, that most utility boilers are equipped with PM control systems and that actual PM emissions from these units are dependent on particle size and the control technology used.

McElroy et al.[36] present particle collection efficiencies for two coal-fired units equipped with a fabric filter baghouse and an electrostatic precipitator, respectively. Their measurements indicate the baghouse produced PM collection efficiencies of >99% over the entire range of particle diameters examined (0.02–10 μm). However, PM collection efficiencies for the electrostatic precipitator were >90% for most particle diameters, and between 80 and 90% for particles between 0.1 and 0.3 μm diameter. This characteristic minimum in particle collection efficiency is typical for particles between 0.1- and 1.0-μm diameter and was also seen in the baghouse data to a lesser extent. Particles in this size range contain neither the mass (momentum) to be removed by impaction nor the high diffusion velocities necessary to migrate to collection surfaces. While most large utility boilers have some kind of PM control, smaller industrial and institutional boilers (often burning residual fuel oils) are much less likely to have such controls. Additionally, these small boilers are often located within urban airsheds.

PSDs

Figure 2 presents representative particle volume distributions for the three coals and oil combustion in the fire-tube boiler (open circles) and refractory-lined combustor (shaded circles). The inset shows more detail in the ultrafine particle size range below 0.1 μm. Together, these

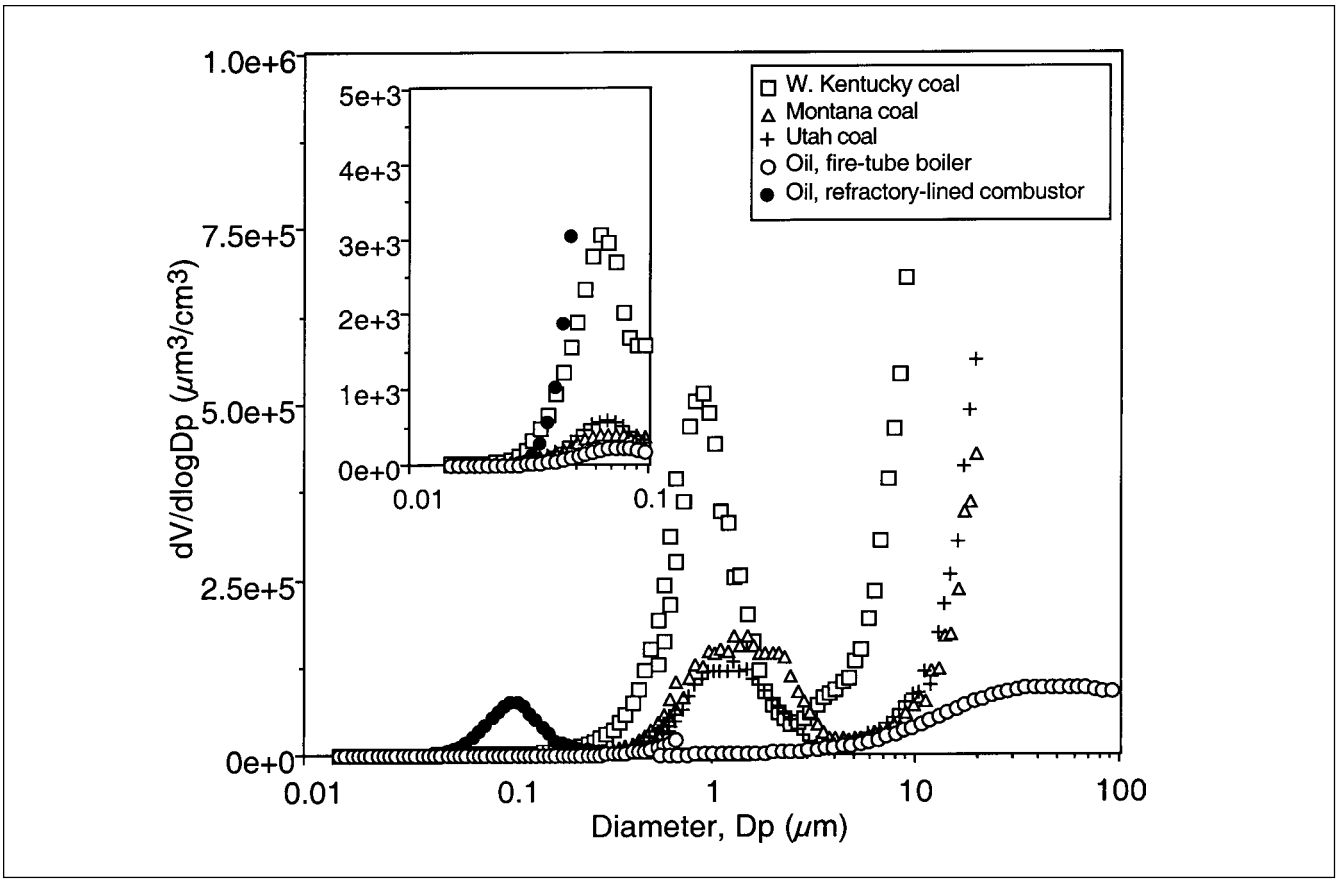

Figure 2. Measured volume PSDs. PSDs between ~0.01 and 1.0 μm diameter were determined by electrical mobility measurements. PSDs greater than ~0.5 μm diameter were determined by light-scattering and time-of-flight measurements.

electrical mobility, time-of-flight, and light-scattering measurements span four decades of particle diameter (0.01–100 μm). The fire-tube boiler and refractory-lined combustor oil PSDs are the same data as plotted in Miller et al.[15] and Linak et al.,[16] respectively. The fire-tube boiler PSDs indicate that most of the particle volume is associated with large (coarse mode) particles >10 μm diameter. The open circle symbols in the inset show that even the fire-tube boiler produces a small accumulation mode with a mean diameter of between 0.07 and 0.08 μm, but that this accumulation mode is much smaller than that for the refractory-lined furnace (shaded circles). Thus, both configurations produced an ultrafine mode, but only the fire-tube boiler produced a bimodal PSD with a very large and dominant coarse mode.

In contrast, the three coals each produce trimodal PSDs. These include small accumulation modes between 0.07 and 0.08 μm, large coarse modes from 7 to 10 μm, and a central mode between 0.8 and 2.0 μm. Unlike the in situ light-scattering technique used during the oil tests, the APS used during the coal combustion experiments does not extend beyond 20 μm. While the accumulation and coarse modes can be described by mechanisms of trace element vaporization, nucleation, and particle growth and residual ash fragmentation, respectively, the mechanisms that produce the central mode are less clear. Model predictions[6,7,16] indicate that coagulation of nucleated vapor cannot produce particles as large as 1-μm diameter. These particles are more likely the result of mineral inclusions that are liberated during the fragmentation and burnout of the coal char particle. This mechanism has been proposed previously to explain supermicron particle formation.[37]

Smith et al.[38] proposed that the presence of cenospheres and plerospheres indicate that a bursting mechanism may be involved. They suggested that gas evolution during rapid heating causes ballooning of some large liquid ash particles. At temperatures slightly higher than that required for cenosphere formation, the viscosity of the liquid particle will be sufficiently small that the particle will burst, releasing a shower of smaller particles. Helble and Sarofim[39] examined the influence of fragmentation on ash PSDs. They measured a mode between 1- and 5-μm diameter which comprised ~25% of the total ash mass and suggest that particles in this size range are formed by perimeter fragmentation of the char during conditions of external diffusion-controlled reaction and excess air.

Baxter[40] also developed a char fragmentation model to predict fly ash PSDs (>0.6 μm diameter) during pulverized

coal combustion. Results indicate that the fly ash PSD is sensitive to both the extent and mechanism of fragmentation. For high rank coals, more fly ash particles of ~2- and 15-μm diameter are produced as a result of fragmentation than any other sizes, and predicted PSDs indicate modes at ~2 and 15 μm, which are qualitatively consistent with those presented in Figure 2. The model also predicts that fragmentation is much less important for lignite fuels. Previous reports of trimodal PSDs for coal fly ash are somewhat limited, and may be a consequence of limited ranges of particle diameters examined, improved resolution of current instrumentation, and field data taken downstream of PM control devices, which are very effective in controlling larger particles. McElroy et al.[36] present composite impactor PSDs from a small 25-MW coal-fired boiler. Their PSDs indicate modes at ~0.08-, 2-, and >10-μm diameter comparable to those presented in Figure 2. More recently, Seames and Wendt[41] have also seen evidence of trimodal PSDs during combustion of an Illinois no. 6 bituminous coal in an uncontrolled laboratory-scale combustor using a low-pressure impactor.

The bimodal PSDs seen for the oil experiments are consistent with a mechanism of metal vaporization/nucleation/coagulation/condensation and incomplete burnout of residual fuel cenospheres.[15,16] SEM images of oil char collected from the fire-tube boiler showed a sponge-like morphology that clearly suggests swelling and extensive pore formation. In general, the extent of ash (metal) vaporization is dependent on carbon burnout. For incomplete combustion, a substantial fraction of the trace metals remain trapped in the unburned char particles, and never escape into the vapor phase. However, as the combustion gases cool, those metals that have vaporized will condense on existing surfaces or, if supersaturation partial pressures are large enough, will nucleate to form new particles. The distinctive submicron peak (between 0.07- and 0.08-μm diameter) is clearly indicative of particles formed by nucleation, coagulation, and condensation of materials that have vaporized. Thus, when large portions of the metal constituents fail to vaporize (open circles), the accumulation mode will be much smaller than when they do vaporize (shaded circles).

The refractory-lined combustor volume PSD (shaded circles) consists exclusively of a narrow submicron accumulation mode with a mean diameter of ~0.1 μm, and both light-scattering measurements and the lack of any cyclone catch containing gray or black particles with measurable LOI support this. Clearly, as the oil char is consumed, the metals have vaporized almost completely and have subsequently nucleated and grown to form the distinctive accumulation mode shown in Figure 2. Comparison between the areas under the submicron volume PSD for the two types of equipment suggests that, while only a very small fraction (<1%) of the metal trace elements are vaporized in the fire-tube boiler, well over 99% of these constituents vaporize in the refractory-lined combustor.

In contrast to residual oils whose ash is almost exclusively bound inherently within the organic molecular structure, very little coal ash is inherently bound. Rather, large fractions of ash components in coal are present as mineral inclusions within the coal particles or as excluded materials, either liberated inclusions during the grinding process or extraneous material collected during mining.[6] As a result, the nature and behavior of coal ash is very different compared with oil. Coal refractory elements, including Al, Ca, and Si, are not easily vaporized and can act to bind otherwise volatile species. Typically, large fractions of coal ash remain in the coarse size fractions with only very small amounts (<1%) vaporizing to produce the accumulation mode. However, the central mode near 1-μm diameter (see Figure 2) indicates that fine PM (including transition metals) may be produced from coal combustion by mechanisms other than vaporization. Interactions between alkali metals and Al- and Si-containing species in coal have been studied by Gallagher et al.,[42] who examined such processes for Na and K with implications for understanding and controlling boiler fouling processes. Additionally, several studies have purposely introduced Al-, Ca-, and Si-based compounds to adsorb toxic trace elements, including Pb and Cd, in waste incineration processes.[26,43,44]

Figure 3 presents mass distribution data for the three coals determined by gravimetric analysis of in-stack and extractive low-pressure cascade impactors. While not as resolved or sensitive as the electronic measurements presented in Figure 2, these data indicate the same qualitative information, including a large coarse mode from 8 to 10 μm and a central mode between 1 and 5 μm. Figure 4 presents the elemental mass fraction distributions of several selected transition metals determined by XRF analysis from a set of MOUDI samples for the western Kentucky coal. These mass fraction data have been normalized by dlogDp to correct for differences in cut-off diameters that might otherwise skew the distribution. However, as a result of this normalization, the data from the first (>10 μm) and last stages (<0.056 μm) are lost. Figure 4 indicates that the trace element mass fraction distributions have the same qualitative behavior as the western Kentucky volume distribution presented in Figure 2; that is, a small accumulation mode ~0.1 μm and a central mode ~1 μm. The data also indicate that transition metals comprise a portion of the fine PM produced during coal combustion. These elemental PSDs (Figure 4) are also qualitatively similar to those presented by Kauppinen and Pakkanen[45] from a utility-scale pulverized coal boiler burning a Polish

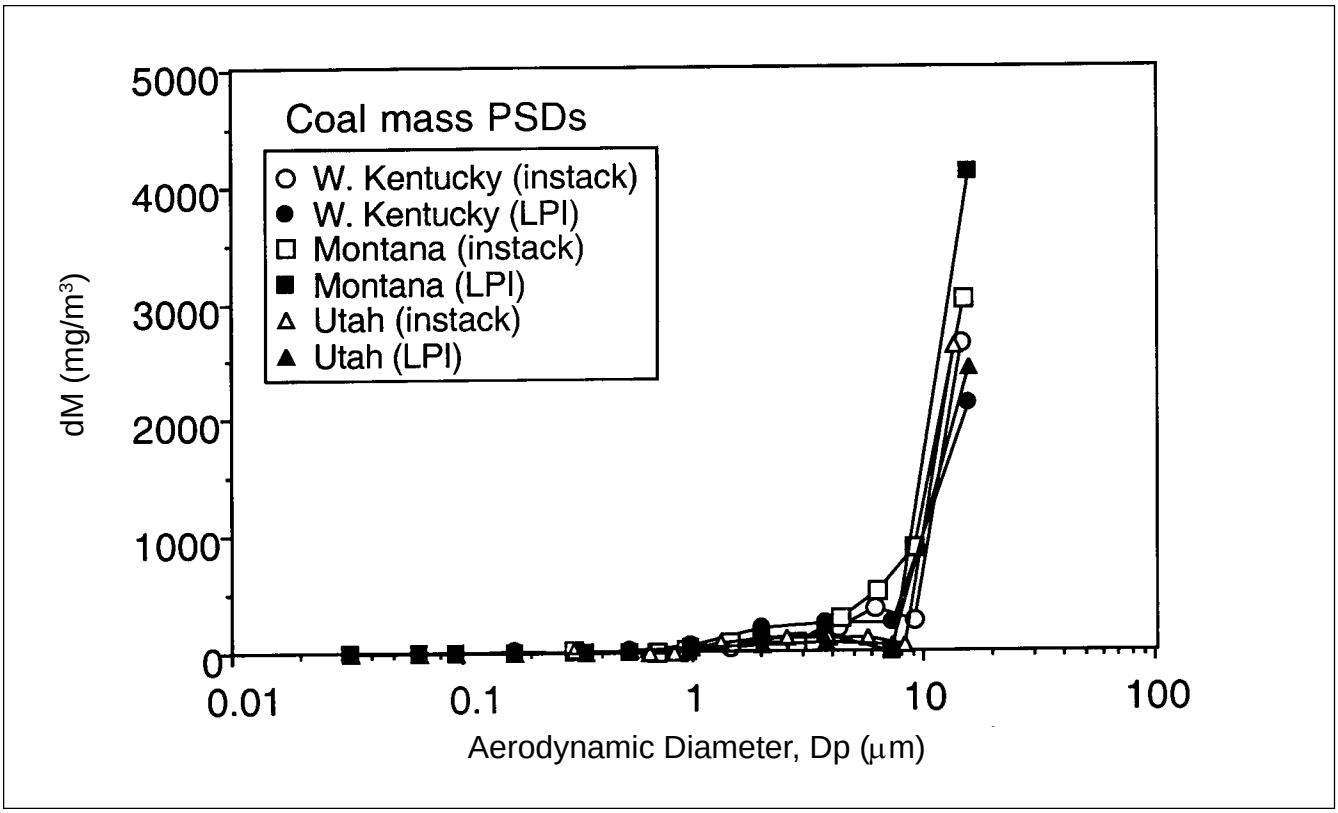

Figure 3. Measured coal mass PSDs.

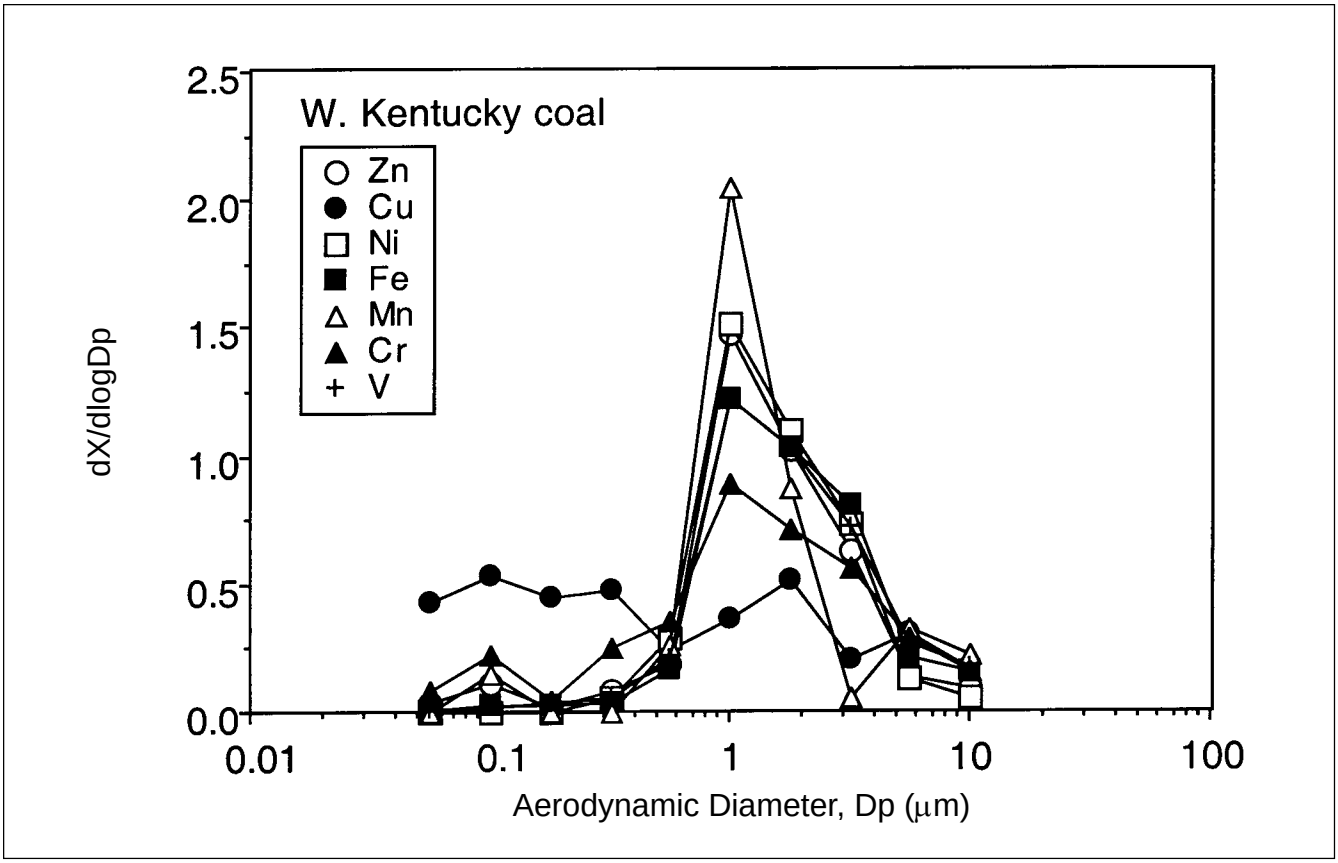

Figure 4. Elemental PSDs for the western Kentucky coal.

coal. Their measurements, taken downstream of the electrostatic precipitator, indicate total mass emissions of 24.3 mg/Nm^3, of which 1.2 mg/Nm^3 (~5%) was comprised of the transition metals Zn, Cu, Ni, Fe, Mn, and V (Cr was not measured).

Successive Leaching

Based on the hypothesis that soluble forms of transition metals may play important roles in the mechanisms resulting in adverse health effects, research was initiated to examine and compare the relative solubility of these elements from different fly ash matrices. This approach, based on a procedure of successively leaching fly ash samples with acids of increasing strength, was briefly described earlier and remains under development. The intent is to compare the relative solubility of these metals from different ash matrices to various health effect end points determined for the same ash samples by colleagues within EPA's National Health and Environmental Effects Research Laboratory. Figure 5 presents results comparing the relative solubility of five transition metals from the $PM_{2.5}$ fraction of fly ash samples from the residual fuel oil and the three coals examined to date. Note, however, that the residual fuel oil fly ash used for these analyses was collected from a third in-house liquid fuel combustor designed to simulate a water-wall package boiler. These samples were collected during a test campaign to examine the combustion characteristics of an Orimulsion fuel and compare its emissions to those of a residual fuel oil.[46] Nonetheless, the package boiler simulator produced fly ash with 38% LOI. This value is higher than that for the refractory-lined combustor, but notably lower than that of the fire-tube boiler (see Table 2), and is consistent with the moderate heat transfer and quench rates associated with this boiler design.

Figure 5 indicates that several of the transition metals associated with the $PM_{2.5}$ ROFA are readily soluble even in water, but these same metals are relatively insoluble from each of the three $PM_{2.5}$ coal fly ash samples. The data indicate that, compared to the oil fly ash sample, strong acids are necessary to dissociate these metals from the coal fly ash. Another interesting result seen in Figure 5 is that not all of the transition metals have similar solubilities in each of the acids. The residual oil data show Ni is almost completely soluble in water, while V and Cu are partially soluble and Zn and Fe are only minimally soluble. Stronger acids are necessary to dissolve these elements. This may be related to the nature of the trace element speciation with the fly ash and may influence the potential bioavailability of the transition metal. The relative insolubility of these metals from the coal fly ashes is likely the result of the mineral nature of coal ash and large quantities of Si, Al, and Ca that are known to interact with trace metals to form relatively insoluble alumina, silica, and calcium complexes. It should be re-emphasized that this leaching process is only intended to determine the relative solubility of different trace elements in different ash matrices. It is not intended to simulate any actual in vivo process. Other work has shown that transition metal mobility may be increased by the presence of organic chelating compounds.[47,48]

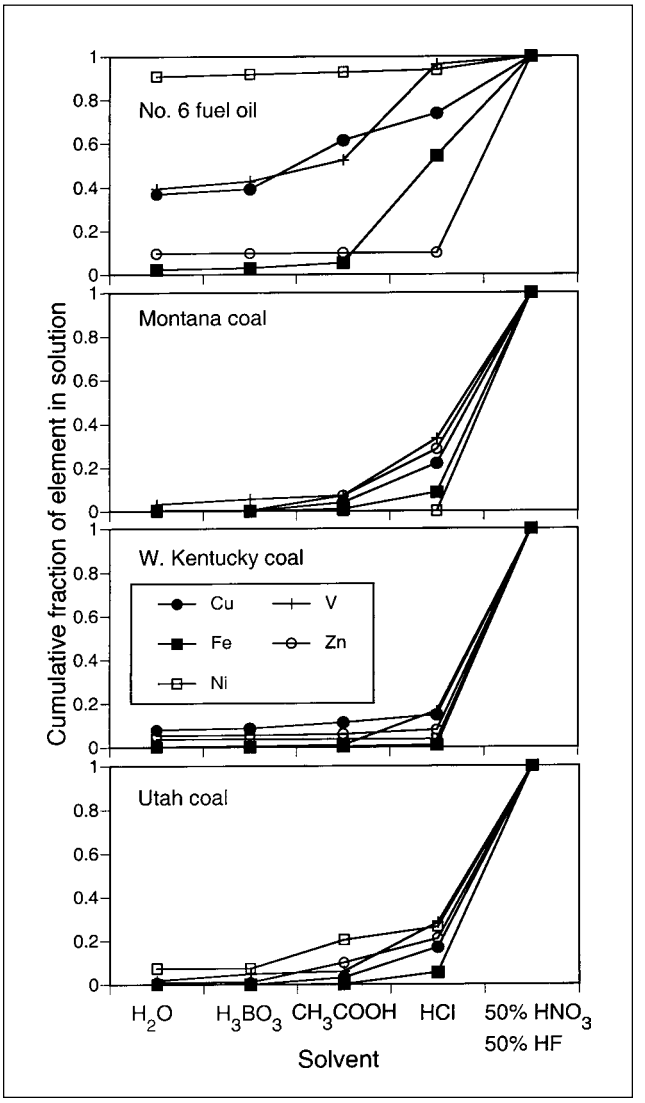

Figure 5. Elemental solubility by successive leaching of $PM_{2.5}$ fly ash.

CONCLUSIONS

Fine particle emissions from residual fuel oil and pulverized coal combustion were examined and compared. A laboratory-scale refractory-lined combustor, which was shown to simulate combustion conditions of a large utility residual oil-fired boiler (as far as particulate emission factors were concerned), produced fly ash particles with an essentially unimodal PSD with a mean diameter of ~0.1 μm. Conversely, a pilot-scale fire-tube package boiler produced particles with a weak bimodal size distribution,

which included a small fraction (~0.2%) of the mass with particle diameters below 0.1 μm and a large fraction (~99.8%) of the mass with particle diameters between 0.5 and 100 μm. Here the large particles were shown to consist of large porous carbonaceous cenospheres resulting from poor carbon burnout, a characteristic not uncommon for that class of equipment. Although the total particulate mass concentrations in the flue gas of the refractory-lined combustor were less than half those of the fire-tube boiler, ultrafine particle concentrations of the refractory-lined combustor were notably larger than those measured for the fire-tube boiler. Volume PSDs obtained from two independent particle-sizing instruments were, with only a few very reasonable assumptions, consistent with independently measured total mass emission rates for both equipment types.

Three pulverized coals burned in a laboratory-scale down-fired combustor produced trimodal PSDs. Uncontrolled mass emissions for these coals were over 20 times higher than those for the residual fuel oil. However, most of this mass contributes to a large coarse mode with only 4–7% of this mass associated with $PM_{2.5}$.

The results presented here provide insight into mechanisms of fine particle formation from residual oil and pulverized coal combustion. For the refractory-lined combustor burning residual oil, where very few large particles were formed, the PSD was nearly unimodal with a mean diameter of ~0.1 μm. These particles were composed primarily of trace species containing Cu, Fe, Ni, V, Zn, and S. Additionally, these particles contained very little carbon (based on LOI), and the particulate-bound sulfur was speciated almost exclusively as sulfates. The weak bimodal behavior of the PM generated by residual oil combustion in the fire-tube boiler produced a fine mode (composed predominantly of metals and sulfur) with a mean diameter of ~0.7–0.8 μm, and a broad coarse mode (comprised primarily of char) with a mean diameter of ~40–50 μm. Both of these types of behavior provide circumstantial evidence for a mechanism of fine particle formation from residual oil combustion. Commonly considered nonvolatile metals are likely released into the gas phase during the last stages of carbon burnout, and because of incomplete carbon burnout, the accumulation mode for particles formed from vapor nucleation was very small for the fire-tube boiler. For the refractory-lined combustor, where char burnout was nearly complete, most of the nonvolatile metals were released into the gas phase.

For the coal experiments, the unburned carbon and LOI ranged from 0.5 to 11.0% and 2.0 to 15%, respectively. While slightly high, these values are not atypical of many utility-scale boilers. The coal PSDs indicate a small accumulation mode ~0.1-μm diameter and a large coarse mode beginning ~10-μm diameter. Similar to the oil PSDs, these modes are consistent with mechanisms involving gas-to-particle formation and growth and residual inorganic ash remaining after char burnout. However, unlike the oil PSDs, the coal data indicate a third central mode between 0.8- and 2.0-μm diameter. Particles of this size are too large to be the result of gas-to-particle growth processes, and are more likely the consequence of micron-scale mineral inclusions liberated during char fragmentation and burnout. This provides a mechanism for refractory transition metals to contribute to $PM_{2.5}$ without the necessity of passing through a vapor phase.

Successive leaching of the $PM_{2.5}$ fly ash from the different fuels may prove to be a useful technique to provide insight into mechanisms controlling elemental speciation, partitioning, and bioavailability. Preliminary results using five acidic solvents of increasing strengths indicate that five transition metals associated with coal are relatively insoluble in all but the most aggressive acids. Conversely, several of these metals associated with ROFA were readily or partially water-soluble. These results may have important implications in the determination of what particle characteristics play significant roles in causal mechanisms of pulmonary damage associated with exposure to fine PM.

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REFERENCES

1. *Particles in Our Air: Concentrations and Health Effects*; Wilson, R., Spengler, J.D., Eds.; Harvard University Press: Cambridge, MA, 1996.
2. *National Ambient Air Quality Standards for Particulate Matter: Proposed Decision*; 40 CFR, Part 50; U.S. Environmental Protection Agency; U.S. Government Printing Office: Washington, DC, 1996.
3. Bachmann, J.D.; Damberg, R.J.; Caldwell, J.C.; Edwards, C.; Koman, P.D. *Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information*; EPA-452/R-96-013 (NTIS PB97-115406); U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1996.
4. Wolff, G.T. *Closure by the Clean Air Scientific Advisory Committee (CASAC) on the Staff Paper for Particulate Matter*; EPA-SAB-CASAC-LTR-96-008; Science Advisory Board: Washington, DC, June 1996.
5. *Fed. Regist.* 62 FR 38652, July 1997.
6. Linak, W.P.; Wendt, J.O.L. Toxic Metal Emissions from Incineration: Mechanisms and Control; *Prog. Energy Combust. Sci.* **1993**, *19*, 145-185.
7. Linak, W.P.; Wendt, J.O.L. Trace Metal Transformation Mechanisms During Coal Combustion; *Fuel Process. Technol.* **1994**, *39*, 173-198.
8. *Review of EPA's Particulate Matter Research Program*; National Research Council; National Academy Press: Washington, DC, 1998.

9. Dreher, K.; Costa, D.; Hoffman, A.; Bonner, J.; Osornio-Vargas, A. Pulmonary Toxicity of Urban Air Particulate Matter (PM). Presented at the A&WMA Meeting on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.
10. Dreher, K.; Jaskot, R.; Richards, J.H.; Lehmann, J.R.; Winsett, D.; Hoffman, A.; Costa, D. Acute Pulmonary Toxicity of Size-Fractionated Ambient Air Particulate Matter; *Am. J. Respir. Crit. Care Med.* **1996**, *153(4)*, A15.
11. Dreher, K.; Jaskot, R.; Lehmann, J.R.; Richards, J.H.; McGee, J.K.; Ghio, A.J.; Costa, D.L. Soluble Transition Metals Mediate Residual Oil Fly Ash Induced Lung Injury; *J. Toxicol. Environ. Health* **1997**, *50*, 285-305.
12. *Fuel Oil and Kerosene Sales 1997*; DOE/EIA-0535(97); Energy Information Administration; U.S. Department of Energy: Washington, DC, 1998.
13. Dockery, D.W.; Pope, C.A.; Xu, X.; Spengler, J.D.; Ware, J.H.; Fay, M.E.; Ferris, B.G.; Speizer, F.E. An Association between Air Pollution and Mortality in Six U.S. Cities; *N. Engl. J. Med.* **1993**, *329*, 1753-1759.
14. Nizich, S.V.; Pope, C.A. *National Air Pollutant Emission Trends Update: 1970-1997*; EPA-454/E-98-007; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, December 1998.
15. Miller, C.A.; Linak, W.P.; King, C.; Wendt, J.O.L. Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler; *Combust. Sci. Technol.* **1998**, *134*, 477-502.
16. Linak, W.P.; Miller, C.A.; Wendt, J.O.L. Fine Particle Emissions from Residual Fuel Oil Combustion: Characterization and Mechanisms of Formation; *Proceeddings of the Combustion Institute;* in press.
17. Cheng, R.J.; Mohnen, V.A.; Shen, T.T.; Current, M.; Hudson, J.B. Characterization of Particulates from Power Plants; *J. Air Pollut. Control Assoc.* **1976**, *26(8)*, 787-790.
18. Bacci, P.; Del Monte, M.; Longhetto, A.; Piano, A.; Prodi, F.; Redaelli, P.; Sabbioni, C.; Ventura, A. Characterization of the Particulate Emission by a Large Oil Fuel Fired Power Plant, *J. Aerosol Sci.* **1983**, *14(4)*, 557-572.
19. Snow, G.C.; Lorrain, J.M. *Evaluation of Innovative Combustion Technology for Simultaneous Control of SO_x and NO_x;* EPA-600/2-87-032 (NTIS PB 87-188926); U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory: Research Triangle Park, NC, 1987.
20. Garg, S. EPA Method 0060–Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes. In *Methods Manual for Compliance with the BIF Regulations: Burning Hazardous Waste in Boilers and Industrial Furnaces*; EPA/530-SW-91-010 (NTIS PB91-120006); U.S. Environmental Protection Agency; Office of Solid Waste and Emergency Response: Washington, DC, 1990; pp 3-1 to 3-48.
21. *U.S. EPA Test Method 1A-Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts*; 40 CFR Part 60, Appendix A; Government Institutes Inc.: Rockville, MD, 1994.
22. *U.S. EPA Test Method 5–Determination of Particulate Emissions from Stationary Sources*; 40 CFR Part 60, Appendix A; Government Institutes Inc.: Rockville, MD, 1994.
23. Galbreath, K.C.; Zygarlicke, C.J.; Huggins, F.E.; Huffman, G.P.; Wong, J.L. Chemical Speciation of Nickel in Residual Oil Ash; *Energy Fuels* **1998**, *12*, 818-822.
24. Galbreath, K.C.; Zygarlicke, C.J.; Toman, D.L.; Huggins, F.E.; Huffman, G.P. Nickel and Chromium Speciation of Residual Oil Combustion Ash; *Combust. Sci. Technol.* **1998**, *134*, 243-262.
25. Huggins, F.E.; Huffman, G.P.; Robinson, J.D. Speciation of Elements in NIST Particulate Matter SRMs 1648 and 1650; *J. Hazard. Mater.* **2000**, *74*, 1-23.
26. Scotto, M.A.; Peterson, T.W.; Wendt, J.O.L. Hazardous Waste Incineration: The In Situ Capture of Lead by Sorbents in a Laboratory Down-Flow Combustor; *Proceedings of the Combustion Institute;* **1992**, *24*, 1109-1118.
27. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Metal Aerosol Formation in a Laboratory Swirl Flame Incinerator; *Combust. Sci. Technol.* **1994**, *101(1-6)*, 7-27.
28. Hillamo, R.E.; Kauppinen, E.I. On the Performance of the Berner Low Pressure Impactor; *Aerosol Sci. Technol.* **1993**, *14*, 33-47.
29. Steele, W.J.; Williamson, A.D.; McCain, J.D. *Construction and Operation of a 10 cfm Sampling System with a 10:1 Dilution Ratio for Measuring Condensable Emissions*; EPA/600-8-88-069 (NTIS PB88-198551); U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory: Research Triangle Park, NC, 1988.
30. U.S. EPA Test Method 3050B. In *Test Methods for Evaluating Solid Waste*; EPA-SW-846; U.S. Environmental Protection Agency: Washington, DC, December 1996; Vol 1A. CD-ROM Version 3, Revision 2, http://www.epa.gov/epaoswer/hazwaste/test/3xxx.htm.
31. Hardesty, D.R.; Pohl, J.H. *The Combustion of Pulverized Coals–An Assessment of Research Needs*; National Bureau of Standards Special Publication No. 561; National Bureau of Standards: Washington, DC, 1979; pp 1407-1415.
32. Walsh, P.M.; Rovesti, W.C.; Fangmeier, B.A.; Markoja, R.L.; Brown, J.P.; Hopkins, K.C.; Lange, H.B.; Freeman, R.F.; Olen, K.R.; Washington, K.T.; Partick, S.T.; Campbell, G.L.; Harper, D.S.; Teetz, R.D.; Bennett, T.E.; Moore, S.P. Size Distribution of Metals in Particulate Matter Formed During Combustion of Residual Fuel Oil. In *Proceedings of the Electric Power Research Institute 1993 Fuel Oil Utilization Workshop*; EPRI TR-103990, Section 3; Electric Power Research Institute: Palo Alto, CA, 1994; pp 132-149.
33. *Compilation of Air Pollutant Emission Factors*; Vol. 2: Stationary Point and Area Sources, 5th ed.; AP-42; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, November 1996.
34. Goldstein H.L.; Siegmund, C.W. Influence of Heavy Fuel Oil Composition and Boiler Combustion Conditions on Particulate Emissions; *Environ. Sci. Technol.* **1976**, *10(12)*, 1109-1114.
35. Goldstein H.L.; Siegmund, C.W. Particle Emissions from Residual Fuel Fired Boilers: Influence of Combustion Modifications; *J. Eng. Power* **1977**, 371-377.
36. McElroy, M.W.; Carr, R.C.; Ensor, D.S.; Markowski, G.R. Size Distribution of Fine Particles from Coal Combustion; *Science* **1982**, *215(4528)*, 13-19.
37. Flagan, R.C.; Friedlander, S.K. Particle Formation in Pulverized Coal Combustion–A Review. In *Recent Developments in Aerosol Science*; Shaw, D.T., Ed.; John Wiley & Sons: New York, 1978; pp 25-57.
38. Smith, R.D.; Campbell, J.A.; Nielson, K.K. Characterization and Formation of Submicron Particles in Coal-Fired Plants; *Atmos. Environ.* **1979**, *13*, 607-617.
39. Helble, J.J.; Sarofim, A.F. Influence of Char Fragmentation on Ash Particle Size Distributions; *Combust. Flame* **1989**, *76*, 183-196.
40. Baxter, L.L. Char Fragmentation and Fly Ash Formation During Pulverized-Coal Combustion; *Combust. Flame* **1992**, *90*, 174-184.
41. Seames, W.S.; Wendt, J.O.L. Partitioning of Arsenic, Selenium, and Cadmium during the Combustion of Pittsburgh and Illinois #6 Coals in a Self-Sustained Combustor; *Fuel Process. Technol.*, in press.
42. Gallagher, N.B.; Peterson, T.W.; Wendt, J.O.L. Sodium Partitioning in a Pulverized Coal Combustion Environment; *Proceedings of the Combustion Institute,* **1996**, *26*, 3197-3204.
43. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Sorbent Capture of Nickel, Lead, and Cadmium in a Laboratory, Swirl Flame Incinerator; *Combust. Flame* **1995**, *100*, 241-250.
44. Davis, S.B; Wendt, J.O.L. Mechanism and Kinetics of Lead Capture by Kaolinite in a Downflow Combustor; *Proceedings of the Combustion Institute,* in press.
45. Kauppinen, E.I.; Pakkanen, T.A. Coal Combustion Aerosols: A Field Study; *Environ. Sci. Technol.* **1990**, *12*, 1811-1818.
46. Miller, C.A.; Linak, W.P. The Influence of Carbon Burnout on Submicron Particle Formation from Emulsified Fuel Oil Combustion; *Fuel*, submitted for publication, 2000.
47. Ghio, A.J.; Stonehuerner, J.; Pritchard, R.J.; Piantadosi, C.A.; Quigley, D.R.; Dreher, K.L.; Costa, D.L. Humic-Like Substances in Air Pollution Particles Correlate with Concentrations of Transition Metals and Oxidant Generation; *Inhalation Toxicol.* **1996**, *8*, 479-494.
48. Smith, K.R.; Veranth, J.M.; Lighty, J.S.; Aust, A.E. Mobilization of Iron from Coal Fly Ash Was Dependent Upon the Particle Size and the Source of Coal; *Chem. Res. Toxicol.* **1998**, *11*, 1494-1500.

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EX 4

CRITICAL REVIEW

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Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health

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ABSTRACT

Particulate matter (PM) emissions from stationary combustion sources burning coal, fuel oil, biomass, and waste, and PM from internal combustion (IC) engines burning gasoline and diesel, are a significant source of primary particles smaller than 2.5 μm ($PM_{2.5}$) in urban areas. Combustion-generated particles are generally smaller than geologically produced dust and have unique chemical composition and morphology. The fundamental processes affecting formation of combustion PM and the emission characteristics of important applications are reviewed. Particles containing transition metals, ultrafine particles, and soot are emphasized because these types of particles have been studied extensively, and their emissions are controlled by the fuel composition and the oxidant-temperature-mixing history from the flame to the stack. There is a need for better integration of the combustion, air pollution control, atmospheric chemistry, and inhalation health research communities. Epidemiology has demonstrated that susceptible individuals are being harmed by ambient PM. Particle surface area, number of ultrafine particles, bioavailable transition metals, polycyclic aromatic hydrocarbons (PAH), and other particle-bound organic compounds are suspected to be more important than particle mass in determining the effects of air pollution. Time- and size-resolved PM measurements are needed for testing mechanistic toxicological hypotheses, for characterizing the relationship between combustion operating conditions and transient emissions, and for source apportionment studies to develop air quality plans. Citations are provided to more specialized reviews, and the concluding comments make suggestions for further research.

INTRODUCTION

Combustion of coal, biomass, and petroleum-based fuels generates particulate matter (PM) ranging from millimeter-sized cinders and soot aggregates to ultrafine nuclei-mode primary particles only a few nanometers in diameter. The largest particles are removed in the combustion zone as bottom ash or wall deposits, or are collected in the post-combustion gas cleaning devices. The smaller particles travel with the combustion exhaust gas and contribute to ambient air pollution on both the urban and regional scale. Epidemiologic studies reported a correlation between adverse health effects and increases in ambient particulate concentration, even when the mass concentration was below the then-current air quality standards. This correlation motivated a call for stricter air quality regulations even though a toxicological mechanism linking small increases in ambient PM and biological responses is still unavailable. Particles smaller than 2.5 μm ($PM_{2.5}$) consist of the tail of the coarse-mode particle size distribution generated by mechanical processes and finer particles that are formed from gas-phase precursors by nucleation, condensation, and surface reaction on other particles, followed by particle growth from coagulation and other transformations in the atmosphere.

This review focuses on the submicron inorganic ash and soot produced by practical combustion systems because the processes by which these particles are produced have been extensively studied over the three decades since the passage of the U.S. Clean Air Act. Metal-enriched ash, soot, and ultrafine particles remain a concern for combustion researchers because these particles have been the focus of mechanistic toxicological hypotheses. Fundamental relationships are presented to show how the primary combustion particle size, morphology, and composition are determined by combustion conditions and the post-flame cool down. The implications of these fundamental relationships are illustrated by descriptions of the results of particle characterization studies from specific combustion applications. The relationships between the ability to measure particle characteristics, both at sources and in the atmosphere, the development of health effects hypotheses, and the development of regulations will be discussed. Examples illustrate recent progress and suggest areas for further work.

The epidemiology and toxicology of ambient PM is an active area of research. Recently, efforts in finding the causes of adverse health effects of particles have intensified.

Accumulating evidence suggests that mass concentration is not the most appropriate measure of potential health effects,[1] and that health studies need to consider other characteristics, such as particle number, particle morphology, and detailed chemical speciation.[2–4] The active toxicological hypotheses have been summarized into the following groups.[5] Some of these, such as mass, are listed based on the epidemiologic studies; others because there are known causal relations with health. There is no hierarchy to the listing.

(1) *PM Mass Concentration*. The initial epidemiologic studies correlated effects with mass as measured by ambient monitoring procedures. The mass concentration of individual chemical species in PM represents the maximum possible dose.

(2) *PM Particle Size/Surface Area*. Stronger associations are seen with fine particle mass, and the body interacts with the surface of an insoluble particle, not with the volume.

(3) *Ultrafine PM*. Particles smaller than 0.1 μm dominate the total number of particles in urban aerosols. Ultrafine particles are deposited deep in the lung by diffusion and can enter the body through the layer of cells lining the alveoli (air sacks) of the lung.

(4) *Metals*. Transition metals including Fe, V, Cu, and Ni act as catalysts in the formation of reactive oxygen species (ROS) and are associated with the activation of many biochemical processes.

(5) *Acids*. Inhalation studies have shown toxic responses that are associated with the amount of H^+ delivered to respiratory surfaces.

(6) *Organic Compounds*. Volatile and semi-volatile organic chemicals associated with particles can act as irritants and allergens. Many aromatic compounds are suspected mutagens or carcinogens and may have acute effects as well.

(7) *Biogenic Particles*. Pollen, spores, and proteins are known allergens. Ambient PM also includes viable bacteria and viruses, biologically generated toxins, and natural organic aerosols. Most pollen is larger than 10 μm, spores are typically 2–10 μm, bacteria are 0.5–20 μm, and viruses are submicron particles.

(8) *Salt and Secondary Aerosols*. Soluble salts formed by ocean spray and by gas-to-particle conversion are thought to be relatively benign. However, since secondary aerosols form a large part of the aerosol mass, the resulting particle mass is indirectly implicated by epidemiologic studies.

(9) *Peroxides*. Ambient peroxides associated with particles may be transported into the lung and may cause oxidant injury.

(10) *Soot*. Carbon black, a surrogate for elemental carbon (EC) in soot, causes tissue irritation and the release of toxic chemical intermediates from scavenger cells in laboratory studies. Soot particles also act as carriers for the organic compounds mentioned in hypothesis 6.

(11) *Cofactors*. The combination of two or more pollutants may cause greater or different effects than the individual pollutants acting separately.

Many of these particle classes or characteristics directly or indirectly involve combustion emissions. This review will emphasize particles containing transition metals, ultrafine particles, and soot because the formation of these types of particles during combustion can be explained by the oxidant-temperature-mixing history of the combustion and gas cleaning processes.

Figure 1 illustrates the main topics covered in this review. An overview of the fundamentals of particle formation in combustion, using coal combustion as a well-studied example, is followed by a discussion of the differences between the PM exiting the combustor and the emissions to the atmosphere. The PM emission characteristics from practical combustion applications, including chemical composition and size distribution, will be reviewed to identify sources of available data. The relationship between specific characteristics of combustion-generated particles and recent work in PM epidemiology, toxicology, and cell biology will be summarized to show the interaction between combustion engineering and the life sciences in addressing questions of public importance. Next, the current U.S. regulations regarding ambient PM will be discussed since the regulatory timetable is driving the need for parallel advances in both health- and engineering-related research. The particles emitted to the atmosphere differ from the particles created in combustion because of size-selective removal and other transformations in any air pollution control devices (APCDs), and examples will be given of studies that have integrated between the combustion and atmospheric emissions research communities. Finally, the need for advances in the ability to conduct time-, size-, and chemically-resolved investigations of fine particles both at combustion sources and in the ambient air will be discussed to illustrate how health studies, air pollution regulations, and control technology all depend on advances in what can be measured.

This paper will focus on the $PM_{2.5}$, PM_1, and ultrafine particles that are emitted as solids from mobile and stationary combustion sources. While combustion emissions of nitrogen and sulfur oxides are of importance from the standpoint of secondary particle formation (nitrates and sulfates), these gas-phase emissions and the subsequent atmospheric transformations will not be discussed. Post-combustion gas cleaning, atmospheric chemistry, and airway

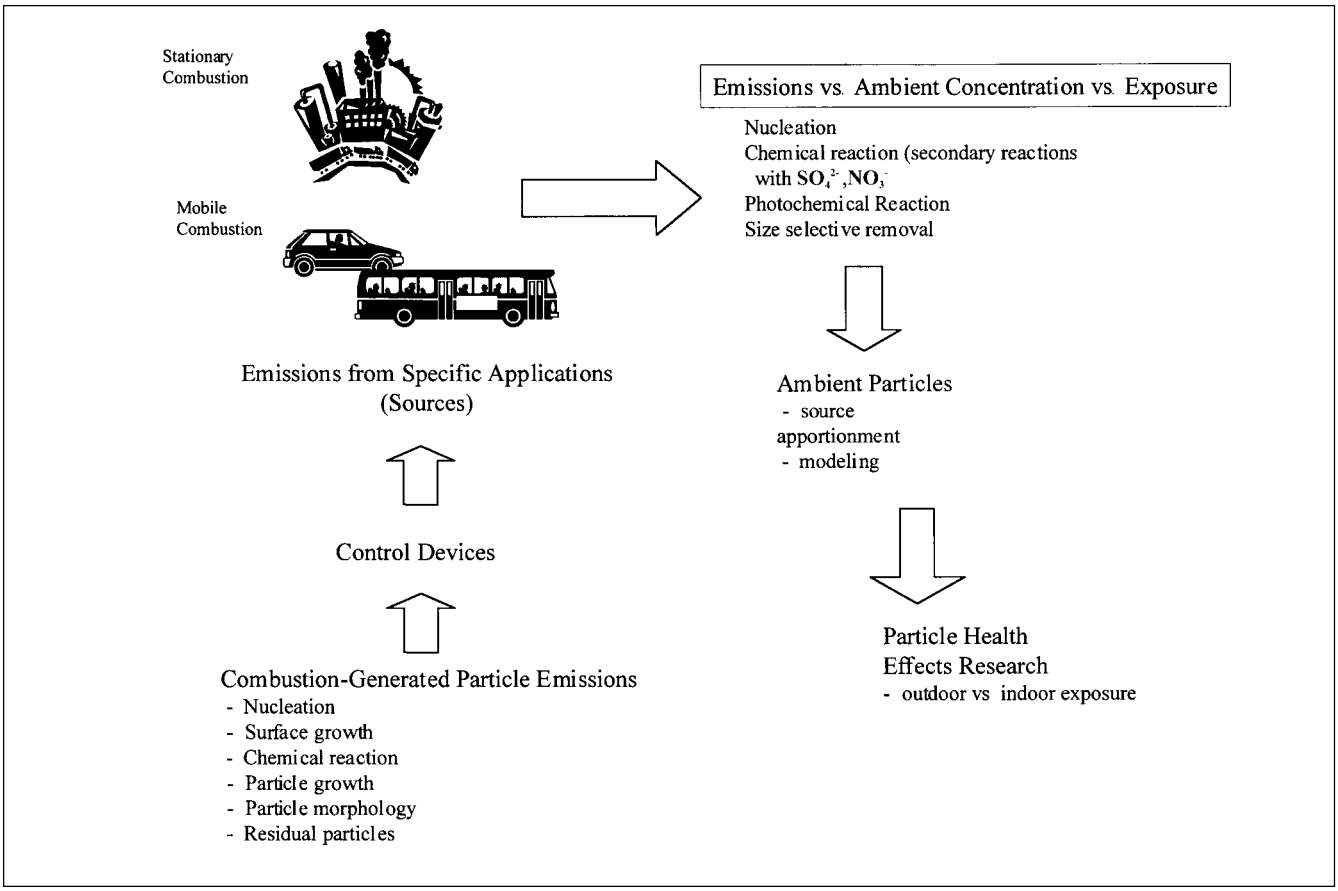

Figure 1. Roadmap to the particle formation and health effects topics discussed in this review.

deposition will also not be discussed in depth even though these processes all modify the characteristics of the aerosol as it travels between the combustion source and the site where the particles interact with the human body.

The following definitions are used in this paper: PM_{10}, $PM_{2.5}$, and PM_1 refer generically to particles with an aerodynamic diameter smaller than 10, 2.5, and 1 μm, respectively, and not specifically to the ambient particle mass as measured by federal reference test methods. Ultrafine particles refer to particles smaller than 0.1 μm, but it should be noted that the older literature occasionally used a larger size as the definition for ultrafine PM. Nanoparticles will refer to particles smaller than 0.01 μm (10 nm). Primary particles, as used in this paper, will be restricted to the roughly spherical structures of inorganic or carbonaceous condensation aerosols that make up aggregate particles. The term primary particles is also used in atmospheric PM research to refer to particles that are collected on filters at the source in contrast to secondary particles formed in the atmosphere from gas-phase precursors. Atmospheric chemistry references[6,7] cover secondary particle formation in detail. The term nuclei will be reserved for the nanometer-sized particles initially formed from gas-phase precursors. Accumulation mode will refer to the 0.1- to 1-μm particles that have long lifetimes in suspension because both diffusion and inertial removal mechanisms are slowest in this size range. The term nucleation mode, as used in the literature, often refers to transient concentrations of submicron particles, which are nuclei that have undergone significant additional growth by condensation and surface reaction. Depending on the context, these particles will be referred to either as a transient mode, to emphasize their rapid transformation, or as a condensation mode, to emphasize that they are derived from vapor-phase material and not from the solid or liquid residue of the fuel.

FUNDAMENTALS OF COMBUSTION-GENERATED PM

The combustion sources of ambient particles include stationary boilers and furnaces, stationary and mobile internal combustion (IC) engines, fugitive emissions from industrial processing, domestic fires, open burning, and accidental fires. The primary particles consist of inorganic or organic species, or a combination of the two. Combustion aerosols are multimodal. The finest particles are produced by gas-to-particle conversions and form the nuclei, or nanoparticles. These grow by coagulation and surface growth into the "accumulation" mode. The larger

supermicron particles are produced from the inorganic material that remains in the solid or liquid phase with the fuel and is referred to as residual ash PM. The emissions depend on the composition of the fuels, the combustion conditions, and the effectiveness of any gas cleaning devices that are used. The emissions of each class of combustor are sufficiently different to merit separate coverage in this review. However, the principles governing their formation are sufficiently alike to warrant collective treatment in this introductory section.

The extensive literature on particle formation and emission, based on both laboratory and field studies, is summarized to show how operating and process conditions affect the size distribution and composition of combustion aerosols. The formation of fly ash from pulverized coal-fired and oil-fired boilers, toxic metal emissions from incinerators, and soot emissions from both stationary combustion and IC engines have been studied extensively and can serve as illustrative examples of the more general processes taking place in all flames. Other important combustion sources of particulate air pollution, such as domestic heating and open burning, are not well characterized compared with large boilers and furnaces or mass-produced engines.

Simplified quantitative relationships give mechanistic insights into the formation of the combustion aerosol under typical conditions. For sufficiently high initial particle number, the evolving size distribution of the submicron aerosol becomes independent of the number of particles nucleated, and the aerosol characteristics can be estimated from algebraic equations. The particle size distribution is determined by the volume fraction of the aerosol that is produced by initial nucleation and by subsequent coagulation and surface growth. Mass transfer limited surface growth can be predicted from the concentration of the condensing species. In multicomponent systems, the growth from condensation and surface reaction can be distinguished by the variation of chemical composition with particle size. The final particle morphology is determined by the ratio of time between collisions and the time for coalescence of the contacting particles.

Particle Inception

There are four classes of particles that form from gas or vapor precursors in combustion systems:

- inorganic particles produced at high temperatures,
- H_2SO_4 produced at exhaust temperatures,
- soot produced at high temperatures, and
- condensable organic particles produced at exhaust temperatures.

Three of these, inorganic ash particles, H_2SO_4 droplets, and condensable organics, involve homogeneous or heterogeneous nucleation. The total amount of condensation for these three categories is well defined, being approximately equal to the amount of initially vaporized material that is in excess of equilibrium at the ambient temperature. For soot, both the nucleation step and the amount of soot are determined by detailed kinetics rather than by thermodynamic equilibrium.

Particle Inception by Nucleation

The nucleation step involves the transformation of a vapor or liquid to clusters of the vapor "monomer" by a series of reversible steps. The clusters will persist and grow when the free energy change accompanying the phase transformation is negative. The fundamentals of nucleation are covered by Seinfeld and Pandis.[6] They discuss the dynamics of cluster formation and evaporation and the formation of critical size nuclei using both classical theory and more rigorous approaches. The critical size is the boundary between incipient particles that are stable and can continue to grow and unstable clusters that redisperse into the gas phase.

In combustion systems, the nuclei are expected to consist of clusters of relatively few atoms and to be of a size of tenths of nanometers. Due to the Kelvin effect,[8] the saturation vapor pressure increases as the particle size decreases, and extremely high supersaturation ratios are needed to make an organic liquid particle smaller than 10 nm stable. These high supersaturations can occur for EC and for refractory metal oxides. It is likely that much of the reported nucleation of condensable acid or organic aerosols in combustion systems actually involves the growth of inorganic ash or soot nuclei that are smaller than the detection limit of the available instruments, resulting in a sudden increase in measured particle number. The Kelvin effect assumes a continuum model and predicts that saturation pressure goes to infinity as the particle radius goes to zero. However, below a certain number of molecules, certain bulk properties, such as surface tension, are no longer applicable.

The classical theory, which assigns bulk properties to clusters, often predicts a critical nucleation size less than the size of a molecule.[9,10] The classical theory is of value in showing the tendency to nucleate, but not in providing the size of the nuclei. More rigorous approaches are available, such as using density function theory to calculate the free energy of clusters.[11,12] The nucleation steps in combustion will be complicated by the strong temperature and concentration profiles in a flame and surrounding individual burning particles. The calculations of the nucleation rate are further complicated by the mixtures of condensable compounds present in combustion products, since the favored nuclei will be multicomponent[13] and the presence of other particles can lead to heterogeneous nucleation.[6] Fortunately, as pointed out by Flagan

and Friedlander,[14] since the time for the nucleation and growth of particles is small relative to the total residence time in a combustor, the details of the early nucleation steps will, in most cases, have little impact on the final number and size of the inorganic aerosols.

Nucleation versus Surface Growth

The competition between nucleation of new particles and surface growth is an issue whenever combustion products with condensable vapors are cooled in the presence of other aerosols. As the combustion products are cooled, the supersaturated vapors can either condense on the surfaces of existing particles or can form new nuclei. This problem was addressed for pulverized coal combustion by McNallan et al.,[15] who modeled the supersaturation versus time of gases cooling at various rates. They allowed for condensation on the surfaces of existing particles and particle formation according to classical nucleation theory. The criterion for nucleation was the development of the supersaturation partial pressure necessary to yield a nucleation rate of 1 particle/cm^3/sec. Assuming a pre-existing aerosol concentration of 1 g/m^3 of 8 μm particles, which approximates the residual fly ash encountered in pulverized coal combustion, and assuming an initial condition of silica vapors at equilibrium with pure silica at a temperature of 2400 K, they predicted that nucleation of silica vapors will occur at temperature of 2320 K for a cooling rate of 1000 K/sec, or at 2240 K for a cooling rate of 600 K/sec. Nucleation was not predicted to occur at 200 K/sec. They also examined the condensation of Na_2SO_4 and lead vapor and concluded that nucleation would not occur for these compounds in the presence of high-surface-area submicron particles. Cooling rates in the burner region of boilers are above 600 K/sec, so this simple analysis indicates that refractory oxides, such as SiO_2, will condense in the flame zone to produce a high surface area aerosol, which will prevent the subsequent nucleation of trace elements in the colder exhaust gases.

Experiments with pulverized coal in laboratory reactors show that nucleation occurs early in the flame zone for both soot and inorganic particles.[16–20] This is supported by simple treatments of nucleation and growth of particles in a boundary layer.[21–23] More detailed treatment of nucleation in the boundary layer of a growing particle is presented by Peshty et al.,[24] who show that the correct treatment should allow for heat release due to condensation, which tends to suppress the nucleation rate locally.

Temperatures decrease through the convection passes of a steam-generation boiler and on into the stack plume, and a point may be reached where H_2SO_4 is supersaturated. Again, there is the potential to form new particles by nucleation versus deposition on existing particles. This is a concern because H_2SO_4 deposited as a layer on coal fly ash has been shown to accentuate respiratory impairment.[25,26] H_2SO_4 condensation is an issue with both high-sulfur and low-sulfur coals because the deposition of H_2SO_4 on particles by SO_3 injection is used to control the resistivity of fly ash in electrostatic precipitators (ESPs).

Another situation where nucleation versus surface growth is important is H_2SO_4 condensation on soot or metal oxide nuclei and the formation of ultrafine particles in the exhaust of diesel engines. The condensation of the organics in diesel exhaust also has a major impact on the size distribution of PM emissions.[27] The effect of particle transformations during cool-down and dilution on reported size distributions will be discussed in the measurements section.

Particle (Soot) Inception by Chemical Reaction

Soot, unlike the inorganic oxide particles and condensable organic PM, is produced by a sequence of chemical reactions, some of which are essentially irreversible. The chemical reactions result in clusters of increasing molecular weight that grow into the measurable size range where the structures are considered particles. The smallest soot particles that have been observed by electron microscopy are in the range of 1–2 nm.[28,29] A soot particle with a diameter of 1.5 nm and a specific gravity of ~1.8 contains ~160 carbon atoms. For soot, particle inception is defined as the particles first capable of measurement, in contrast to the nucleation process where there is a critical particle size at which nucleation occurs for a particular supersaturation.

The vast literature on soot formation and oxidation has been summarized in various reviews and specialized conferences on soot.[30–35] Despite the large amount of literature on soot, the models of soot formation are still evolving. The three chemical kinetic components of a soot model are particle inception, surface growth, and surface oxidation. Coupled to the chemistry controlling the conversion of molecular precursors into solid soot are the physical models of particle coagulation and coalescence, which determine the soot structure.

Soot forms under fuel-rich conditions in which hydrocarbon fragments have a greater chance of colliding with other hydrocarbon fragments and growing, rather than being oxidized to CO, H_2, CO_2, and H_2O. At equilibrium, soot exists when C/O exceeds 1.0. Soot, however, is observed in flames of premixed hydrocarbons in air at C/O values of between 0.5 and 0.9.[32] In diffusion flames, soot forms even in the presence of excess air, since oxygen-deficient conditions will always be found on the fuel side of the flame front.

The reactions leading to soot are shown schematically in Figure 2, which is based on Bockhorn[30] and others. One

of the critical steps in soot formation is the formation of the first aromatic ring, usually benzene. It is for this reason that fuels having a high aromatic hydrocarbon content form soot easily. This has been described in terms of a threshold sooting index for various classes of organic compounds.[36] Molecular weight growth then proceeds with the formation of polycyclic aromatic hydrocarbons (PAH), which are considered to be precursors to soot. The formation mechanisms proceed either through a sequence of hydrogen abstractions and acetylene addition or by the polymerization of the aromatic moieties that are produced.[37,38] Both mechanisms occur in parallel. Positive ions in the flame have been proposed as the initial nuclei sites for soot particle formation.[37,39]

Particle Growth by Collisions

Once particles are formed by either nucleation or chemical reactions, they will grow by a combination of coagulation and surface deposition. The consequences of coagulation will be treated in this section. For the following analysis, it is assumed that all the aerosol mass originates as n_0 particles of diameter d_0 at a time of zero and that the particles coalesce on each collision. The evolution of the particle diameter with time is readily obtained by applying the continuous coagulation equation[6]

$$\frac{dn(v,t)}{dt} = \frac{1}{2}\int_0^v K\,n(v-q,t)n(q,t)dq - n(v,t)\int_0^\infty K\,n(q,t)dq \qquad (1)$$

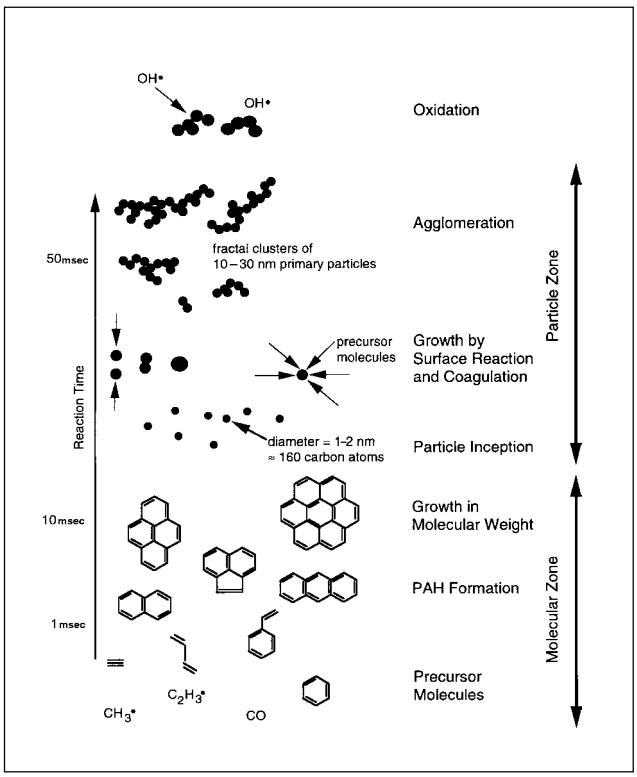

Figure 2. Kinetically limited chemical reactions and physical processes involved in soot formation. Based on Bockhorn.[30]

where $n(v,t)$ is the number of particles of volume v at time t, and K is the collision coefficient, which varies with particle size. Equation 1 is a simplification of the general dynamic equation[40] for the limiting case of no particle sources and no transport into the control volume. The first term in eq 1 corresponds to the production of particles of volume v by collisions of all combinations of smaller particles, $(v - q)$ and q. The second term is the loss of particles out of the size range by collisions with all other particles. This form of the aerosol dynamic equation assumes that the initial particle volume is vanishingly small compared to the system volume ($f_v \approx 0$). Expressions for K are available for the continuum, transition, and free molecular regimes, depending upon whether the particle size is much larger than, comparable to, or smaller than the mean free path of the ambient gas.[40,41]

MAEROS is a widely used numerical code for simulating multicomponent aerosol coagulation. MAEROS solves eq 1 by approximating the polydisperse aerosol with a series of constant size sections.[42] Sectional methods do not accurately model the behavior of the particle nuclei or molecular clusters. Discrete-sectional methods treat molecular clusters as discrete particles, then switch to a sectional approximation for larger particles.[43] Discrete-sectional codes are the most accurate method for numerically solving the aerosol dynamic equation over the entire size spectrum, but these methods are susceptible to problems with numerical diffusion, and care should be exercised in their use.[44] Analytical approximations for solving eq 1 for polydisperse coagulation have been developed by making simplifying approximations, such as by assuming a lognormal size distribution.[45,46] Other methods for calculating multicomponent aerosol dynamics have also been developed.[47–50]

For monodisperse aerosols, $n(v - q)$ is 0, and $n(v,t) = n(q,t) = n$, so eq 1 simplifies to

$$\frac{dn}{dt} = -Kn^2 \qquad (2)$$

The collision rate increases with the square of the particle number concentration and increases non-linearly with decreasing particle size, since K varies with particle size in the transition and free molecular regimes. This equation can be solved to obtain the decay in number concentration as function of time

$$n(v,t) = \frac{n_0}{1 + n_0 Kt} \qquad (3)$$

The characteristic time scale for coagulation, assuming K is constant (valid in the continuum regime), is[51]

$$t_c = \frac{2}{Kn_0} \qquad (4)$$

For $n_0Kt >> 1$, the number of particles becomes independent of n_0, so the details of the initial nucleation rate are not needed to calculate the final aerosol distribution.[14] For a boiler with a residence time of 6 sec to the precipitator, the asymptotic relations will be valid for $n_0 > 10^9$ particles/cm^3. U.S. coals average an ash content of 10%. Typically, on the order of 1% of the ash vaporizes to produce the submicron fume. This yields values of n_0 on the order of 10^{14} particles/cm^3 for 1-nm particles and 10^{11} particles/cm^3 for 10-nm particles. Emission of 0.1% of the fuel as soot will give about the same values of n_0. The coagulation coefficient, K, varies with particle size and with gas temperature, so eq 3 is approximate. However, K varies by less than an order of magnitude over the 10-nm to 1-μm size range, and the initial nuclei number is orders of magnitude higher than that needed to make $n_0Kt > 1$. The limiting formulae will be a reasonable model for the submicron condensation aerosols formed by most stationary combustion systems.

In this limit, if the volume of aerosol formed per unit volume of space is f_v, then the particle diameter $d(t)$ is given by[40]

$$d(t) = \left(\frac{6 f_v K t}{\pi}\right)^{1/3} \tag{5}$$

where K is a constant, given by $8kT/3\eta$, for particles in the continuum regime; k is the Boltzmann constant, and η is the gas viscosity.

For the free molecular or kinetic regime, K is a known function of the particle diameter and velocity. The equation for the rate of change in number density, for this case and a fixed f_v, is given by[33]

$$\frac{dn}{dt} = -\frac{6}{5} k_t f_v^{1/6} n^{11/6} \tag{6}$$

where

$$k_t = \frac{5}{12}\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6kT}{\rho}\right)^{1/2} G\alpha \tag{7}$$

and ρ is particle density; G is the enhancement factor to allow for the van der Waals acceleration factor that is a function of the Hamaker constant,[8,52] and it has a value of about 2; and α is a factor to allow for the particle size distribution, and it has a value of 5.66 for monodisperse particles. The exponent of n of 11/6 in eq 6 versus the exponent of 2 in eq 2 is a consequence of allowing for the dependence of collision rate with particle size and the constraint that f_v is constant.

Friedlander and co-workers showed that, if allowance is made for the polydisperse particles, a self-preserving size distribution is approached.[40,53] For this case, the particles have a narrow size distribution with a geometric standard deviation of 1.37 for the diameter, and the coefficient α has a value of 6.55, not very different from the value of 5.66 for a monodisperse aerosol. Solution of eq 6 for a fixed volume fraction of aerosols f_v then yields the following relations for particle number and particle size:

$$n(t) = \left(k_t f_v^{1/6}\, t\right)^{-6/5} \tag{8}$$

$$d(t) = \left(\frac{\pi}{6}\right)^{-1/3}\left(k_t f_v t\right)^{2/5} \tag{9}$$

The evolution of particles following these approximate equations has been demonstrated in small-scale studies of aerosols formed from combustion systems for fly ash from coal[22,54,55] and soot particles[30,56,57] and waste combustors.[58,59]

As shown by eqs 8 and 9, the number and size of particles can be determined for $n_0kt >> 1$ if the amount of material in the form of the aerosol is known. When f_v is measured from the total amount of submicron ash collected, good agreement is observed between theory and experiment, both for the particle size distribution of the submicron ash[55] and the dependence of the mean particle diameter on f_v.[22]

The value of f_v for the mineral matter is determined by the vaporization kinetics, and is a function of temperature and environment to which the minerals are exposed. The mass of the submicron aerosol is usually dominated by the refractory and alkali metal oxides.[54,60,61] At typical combustion temperatures, the burning rate of a particle is limited by gas-phase diffusion, and the particle is surrounded by a CO-rich reducing atmosphere. The vaporization of the refractory metal oxides is augmented by the reduction of the oxides by CO to form suboxides such as SiO and Al_2O and elemental metals such as Fe, Ca, and Mg. The suboxides and metals will diffuse through the particle boundary layer into the bulk gas where they are oxidized and condense to produce the submicron aerosols. The vaporization rate is strongly temperature-dependent[55,62–64] so that the amount of submicron aerosol will vary with combustion conditions. The vaporization of elements is complicated by their interaction with the minerals in the coal. Sodium, for example, will have its vaporization suppressed either because it may be originally present in sodium aluminosilicates or because it is captured by the alumina silicates after release.[65–67]

Particle Growth by Condensation and Surface Reaction

Vaporized elements distribute on the surfaces of existing submicron and residual ash particles by condensation and chemical reaction. The rate of mass addition to a spherical particle for mass-transfer limited deposition over the entire range of particle size is given by the Fuchs-Sutugin interpolation equation:[6,41]

$$\frac{dm}{dt} = 2\pi c_\infty D d_p \frac{1+Kn}{1+1.71Kn+1.33Kn^2} MW \qquad (10)$$

where c_∞ is the concentration of the condensing species, MW its molecular weight, D its diffusivity, and Kn the Knudsen number, defined as the ratio of the mean free path in the gas to the particle diameter d_p.

For the case in which the rate of deposition is controlled by chemical reaction, the mass flux to the surface is independent of mass transfer and is given by

$$\frac{dm}{dt} = \pi d^2 MW k_s C \qquad (11)$$

where MW is the molecular weight of the depositing species, C is the concentration in the gas, and k_s is the rate of surface reaction. The literature also covers the cases of combined mass transfer and surface kinetics and the additional complication of pore diffusion in porous surfaces.[33,68,69]

Because of the higher surface area per unit mass, smaller particles tend to be enriched in the compounds that condense or deposit on the surface. The trace elements in coal and waste tend to deposit without significantly changing the particle size distribution. For this case, the mass concentration of the depositing species can be readily calculated by integrating the mass deposition of the depositing species along an ash particle trajectory and dividing the mass deposited by the mass of the ash particle, that is,

$$Mass\ Conc(D) = \int_0^t \frac{dm}{dt}\,dt \Big/ \frac{\pi d_p^3 \rho}{6} \qquad (12)$$

Applying eqs 10–12 to the trace elements shows that concentration of trace elements on the surface of the ash can be described as a power function of size, with the concentration increasing as the particle size decreases. The mass concentration dependence upon particle size is therefore proportional to $1/d^n$, where the exponent n for the limiting cases is given in Table 1.

An added case is that of a porous particle with chemical kinetics controlling. For this case, the amount of reaction is proportional to volume, and the concentration of the trace reacting species will be independent of particle size. The dependence will be different for the submicron and supermicron particles since these straddle the gas mean free path in size. The gas mean free path varies from ~0.2 μm at ambient conditions to ~1 μm at combustion conditions, so that ultrafine particles will generally have $Kn >> 1$ and supermicron particles $Kn << 1$. Given that the Kn is the mean free path in the gas (a constant) divided by the particle diameter, eq 10 shows that dm/dt is proportional to d for $Kn << 1$ and to d^2 for $Kn >> 1$.

Table 1. Exponent n in size-dependent mass concentration of trace species: concentration $\propto (1/d^n)$

Controlling Mechanism	Particle Size	Exponent *n*
External Mass Transfer	Ultrafine (Kn >> 1)	1
External Mass Transfer	Supermicron (Kn << 1)	2
External Surface Kinetics	All Sizes	1
Internal Surface Kinetics	All Sizes	0

The early studies on the size-dependent concentration of elements in fly ash[70–72] all were performed for supermicron particles and showed the $1/d^2$ size dependence expected for mass transfer-controlled condensation. Some studies[21,73] have shown the difference in the dependence on particle size of the trace volatile element concentration between the submicron and supermicron fractions. Other studies have shown an enrichment of the smaller particle sizes in the trace volatile elements.[21,54,60,61,66,69–72,74–84]

The reasons for attention to the size dependence of trace element concentration are that (1) this provides a diagnostic for the mechanism of surface deposition; (2) the enrichment of submicron particles in certain elements affects the total capture efficiency of that element in the APCDs; and (3) elemental concentrations affect the chemical speciation, which can be important for health effects.

The exponent n that best fits the variation of elemental concentration with size can be used to determine the mechanism of deposition, for example, whether it is condensation or surface reaction. Haynes et al.[69] deduced from the size dependence of particle composition that the deposition of As and Sb was controlled by chemical reaction. More extensive studies of the size dependence of the deposition have been carried out[85–87] showing that As, Se, and Sb react with the fly ash to an extent that depends on ash composition, thus leading to a coal-dependent partitioning of the elements between the submicron and supermicron ash.

Elements that deposit by surface reaction or surface condensation are expected to be enriched in the surface layers. Studies using surface spectroscopic techniques have shown that the surface layers of both the supermicron[88] and submicron[21] ash particles are enriched in the trace elements. By ion milling of the particles, one can show the stratification that results from the sequential deposition of elements. The implications of this surface stratification to particle toxicology will be discussed later in this review.

To model the partitioning of trace elements in combustion, one needs the particle size distribution of the submicron and supermicron ash and the amount of each of

the trace elements vaporized. Models of the vaporization of trace elements based on equilibrium assumptions[89–91] have been developed for the vaporization and subsequent condensation or chemical surface reaction of trace elements.

The models are based on the assumption of equilibrium between the trace species and the vapor and the residual ash in the combustor. Subsequent condensation and reaction of the trace species is also taken into account. In the model by Sandelin and Backman, two reactors in series are considered to represent the radiant section of a boiler and the ESP, respectively.[90] The partitioning of trace elements in the radiant chamber is calculated for a given fuel composition and fuel/air ratio from equilibrium for an assumed distribution of bottom and fly ash and the temperature of the radiant chamber. The distribution of the elements from the ESP is obtained from the temperature in the precipitator and the ash collection efficiency.

Simulations carried out for a boiler for As, Cd, Hg, Ni, Pb, Se, V, and Zn were found to be in reasonable agreement with experimental observations on an operating power plant. In the paper by Yousif et al., the metal partitioning was calculated by a post processor using input obtained from a computational fluid dynamic simulation of a boiler.[91] The major mass of the ash is distributed between the residual fly ash and submicron ash as inlet conditions. The trace species are assumed to be released at a rate proportional to the char burning rate. The concentration distribution of the trace species is then calculated, allowing for condensation on surfaces and nucleation. The vapor species were assumed to be in equilibrium. Simulations were carried out for Pb and Cd, and their distribution between the residual and submicron ash was found to be in good agreement with experiments on a pilot scale combustor fired with coal and sewage sludge. Nucleation was not found to occur, as the supersaturation did not reach the critical level.

Most studies of trace metals from coal combustion (including some by the co-authors) have reported elemental concentration or enrichment factors since this is what is directly measured by the chemical analysis. Enrichment factor is defined as the concentration of an element in a particular size fraction (e.g., the submicron ash) divided by the average concentration for that element in the total ash. The measured concentration is controlled by the mass balance, and an element may be reported as being depleted in the submicrometer ash solely because of dilution by another element. For example, alkali metals dominate the submicrometer ash from low rank coal, while carbon dominates the particulate emissions from oil and biomass combustion. The raw concentration of transition metals in the total ash from oil combustion is largely an artifact of the combustion efficiency, not a result of the metal vaporization. The relative amounts of elements may be relevant for some health-related studies since the mineral form and valance state of the trace element is often sufficiently described by the equilibrium composition in the bulk ash matrix. For other types of health studies, the absolute amount emitted is of concern. While elemental concentration data is useful, including sufficient data in a publication to calculate a mass balance greatly enhances the value of the particle composition data for reuse in both aerosol formation mechanism and toxicology studies.

Particle Morphology

Soot and submicron ash particles often consist of aggregates of 10–30 nm primary particles. It is important to understand what determines the structure of these particles, since the aggregate size determines the aerodynamic behavior of the particles while the primary particle size determines the surface area.

The coagulation theory described above assumes that particles coalesce on collision. This assumption is valid as long as the coalescence time is short compared with the time between particle collisions. For inorganic particles, coalescence times can be calculated assuming surface tension-driven viscous flow using the theory of Frenkel

$$t_c = \frac{\eta r}{\gamma} \tag{13}$$

where η is the viscosity, and γ the surface tension. Alternatively, the coalescence time can be determined by solid-state sintering[92,93]

$$t_c = \left(\frac{\Delta L}{L_0}\right)^{5/2} \frac{\sqrt{2}kTd_p^3}{160D^*\gamma a^3} \tag{14}$$

where DL/L_0 is the fractional shrinkage in diameter of two spheres, D^* is the self-diffusion coefficient for the mobile species, and a^3 is the atomic volume of a diffusing vacancy. As long as the characteristic coalescence time is much smaller than the time between collisions, the particles will coalesce and maintain their sphericity. The coalescence time increases because of the increase in particle diameter and the decrease in temperature (leading to an increase in η or a decrease in D^*). After a time, which depends on the combustion conditions, the colliding particles will begin to form aggregates. This transition has been studied for coal combustion aerosols and for the flame synthesis of particles.[19,94–96]

The aggregates that are produced have a fractal dimension, D_f, which provides the scaling parameter relating the number of particles n_a in an aggregate to the ratio of the radius of gyration r_g and the primary particle size r_0:[95]

$$n_a \propto \left(r_g / r_o\right)^{D_f} \tag{15}$$

where D_f has values of 3 for a solid sphere and of 1 for a string of particles. For soot and submicron ash particles, the value of D_f is about 1.7.[95,97,98] The theory for the coagulation of aerosols has been extended to aggregates, and a two-dimensional solution was obtained allowing for coagulation and sintering.[99,100] Application of this theory shows the aggregates still assume a self-preserving size distribution but with a wider size distribution than that for spherical particles.

For soot particles, there are several hypotheses for the formation of aggregates.[37,39,101] One of these is that the soot precursor particles are liquid polymers[38] and will coalesce after collision. In parallel, the liquid polymers will dehydrogenate and their viscosity will increase, leading to a transition from coalescence to aggregation similar to that described above for inorganic aerosols. A second hypothesis[37] is that the soot particles form as a solid, then collide and aggregate. Surface growth occurs in parallel with growth by collisions. If the surface growth is sufficiently rapid, the particles in the growing aggregate will be immersed in the deposited carbon and the resulting structure will appear as a spherical particle. Numerical simulations support this hypothesis when realistic values of surface growth and coagulation are used.[37] As the particle size increases, and as the species contributing to surface deposition are depleted, the rate of surface growth due to deposition will decrease. After this point, the soot particles will develop as aggregates with a fractal structure.

The final particle morphology at the exit of the high-temperature zone is the result of multiple processes. The characteristic times for these processes can be readily predicted, and examination of particle morphology gives a good indication of which processes are dominant for the given situation. This type of analysis was applied to the behavior of sorbents for toxic metal control.[102]

Residual Ash Formation

Submicrometer particles dominate the number count of particles emitted by combustion sources and very often dominate the surface area as well, but the mass of PM emissions is usually dominated by the organic or inorganic residue of material that remained in a solid or liquid phase throughout combustion. These particles are referred to as residual ash. The residual ash formation process differs from the formation of the submicrometer particles by molecular weight growth processes for soot and by vaporization and condensation for inorganic ash, as described above. The total amount of noncombustible minerals in the residual ash is determined by the mass balance, and the total amount of carbonaceous material in the residual ash is determined by the combustion efficiency.

Most fossil fuels contain inorganic components. For U.S. coals, this inorganic content constitutes ~10% on average of the mass. For petroleum, the maximum ash mass ranges from 0.05% for a light No. 4 oil to 0.15% for a No. 5 fuel oil; a typical value No. 6 or residual oil ash content is 0.8%.[103] A representative ash content for wood is 2.5%, but it varies widely.

Figure 3 illustrates the major processes affecting the formation of submicron and supermicron ash during the combustion of coal, biomass, and oil.[69,73] The mass of particle emissions measured at the combustion chamber exit is determined by a number of complicating factors. The first is that, depending upon the type of combustor, only a fraction of the total ash content in the fuel is carried over with the combustion gases as fly ash. The so-called bottom ash is deposited in the ash hopper on the floor of a suspension-fired furnace or is dropped off the end of the grate in a stoker-fired furnace. The ash entering the particulate control equipment downstream from coal-fired boilers varies from 10% of the total fuel ash content for cyclone or wet-bottom furnaces to 85% for dry-bottom pulverized coal-fired furnaces. The fly ash particle size distribution is multimodal. The factors that control the residual ash size distribution will be discussed below for the case of pulverized coal-fired systems, partly because pulverized coal has been most extensively studied, and partly because these boilers account for a large portion of the primary energy production worldwide.

The noncombustible matter in pulverized coal includes mineral grains of clays, pyrites, and quartz that vary in size from less than a micron to the largest sizes that can pass through the pulverizers, which is over 300 μm. Part of the inorganic matter is included in the coal matrix as discrete crystals, some is incorporated in the organic matrix as organo-metallic complexes or as ion-exchanged metals bound to the organic acids, and some of the minerals are present as extraneous particles. These forms of inorganic matter are shown schematically in Figure 4.[104] Detailed characterizations of the mineral content of coals have been conducted by computer-controlled scanning electron microscopy (CCSEM) by a number of research groups.[105–111] An example of the mineral size distributions as determined by CCSEM is provided in Figure 5, which shows the size distribution of mineral inclusions in raw Kentucky No. 11 coal. The kaolinite and illite inclusions are found in the smaller particle sizes while calcite and pyrites are in the larger particle sizes. Quartz and mixed silicates are distributed over all size ranges.

Given the mineral distribution within the pulverized coal, one can calculate the ash particle size distribution using a material balance. Assume a coal particle of density ρ_c and diameter d_c, and a mass fraction f_a yields n ash particles of density ρ_a and diameter d_a. A mass balance then yields the

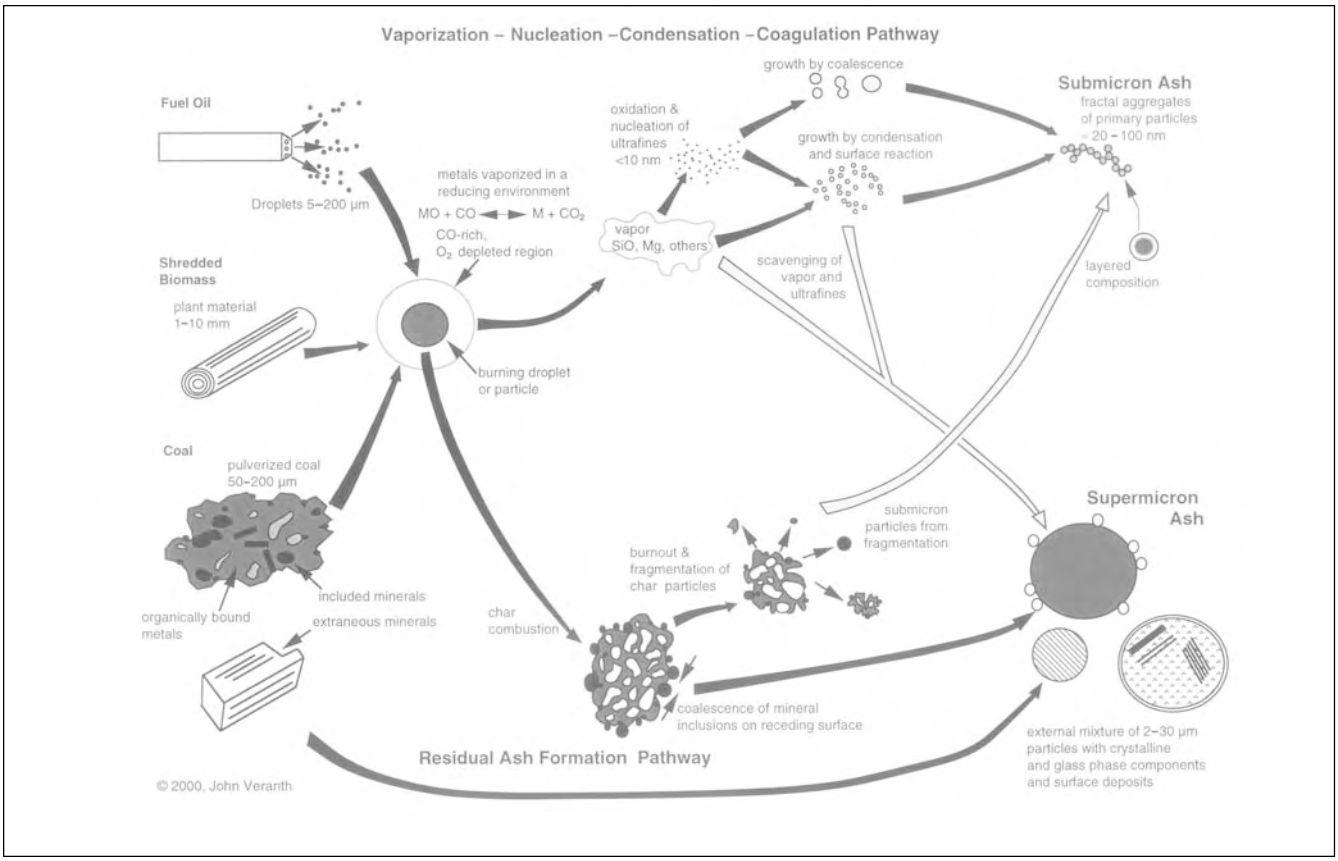

Figure 3. Formation of inorganic submicron and supermicron particles during combustion of solid and liquid fuels. Submicron particles are formed by the vaporization–nucleation–coagulation pathway. Supermicron particles are formed by the residual ash pathway. Based on earlier versions.[69,73]

following expression for the diameter of the ash particle:

$$d_a = d_c\left(\frac{f_a\rho_c}{n\rho_a}\right)^{\frac{1}{3}} \qquad (16)$$

To apply this simplified relationship, assume that the coal specific gravity is constant and equal to 1.3, that the ash specific gravity is constant and has a value typical of glass of ~2.5, and that each coal particle yields one ash particle, that is, that $n = 1$. For these assumptions, a typical U.S. coal with 10% ash ($f_a = 0.1$) yields a ratio of the ash particle diameter to the coal particle diameter, d_a/d_c, of 0.37. A pulverized coal with a mean coal particle diameter of 50 μm would yield a mean ash diameter of ~19 μm

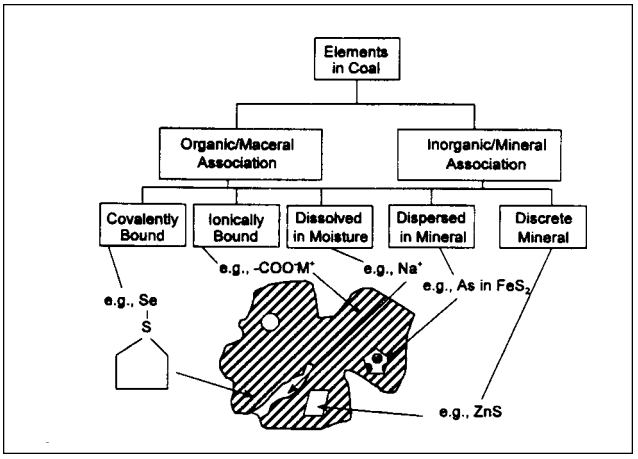

Figure 4. Classification scheme for describing the modes of elemental occurence in coal. Reproduced by permission of Elsevier Science.[104]

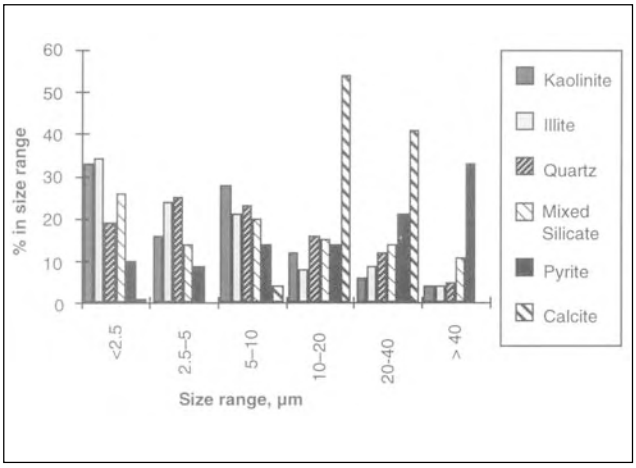

Figure 5. Size distribution of minerals in Kentucky coal. Quartz, kaolinite, and illite are concentrated in the smaller size fractions, while pyrite and calcite are concentrated in the larger sizes. Based on data in ref 111.

under these assumptions. This is a reasonable default value, but the actual transformation mechanisms are more complicated. One needs to account for the different ash content of each coal particle, which will result in variations in both f_a and r_c. The fragmentation of coal char during combustion and the incomplete coalescence of mineral droplets on the shrinking surface both yield values of n other than unity. Also, the ash particle density ρ_a varies due to changes in composition of individual ash particles and to the presence of gas bubbles within the ash.[112–114]

The mineral inclusions are not distributed evenly between different coal particles. Some particles are nearly inclusion-free and some of the particles are pure minerals (the extraneous ash). The actual distribution of the minerals between the different coal particles is provided by CCSEM.[109,115] If such information is not available, an approximate distribution can be obtained by assuming that the minerals are randomly distributed between coal particles.[116–119] The ash particles will have a particle-to-particle variation in composition that will reflect the variation in the mineral content of the individual coal particles from which they are produced. This is illustrated in Figures 6 and 7, which show the Al, Si, and Fe distributions both in the parent coal minerals and in the resulting fly ash, respectively.

The number of ash particles, n, produced by a coal particle will depend upon the competition between coalescence of molten mineral inclusions and fragmentation of the char particle during combustion. The ash produced by the mineral inclusions in coal will adhere to the char surface as it burns and will coalesce with other ash particles as the char surface recedes.[120] The fragmentation of chars has been shown to depend upon the macroporosity of the chars[114] and therefore upon the swelling behavior of coals, dependent upon coal-specific pyrolysis behavior.

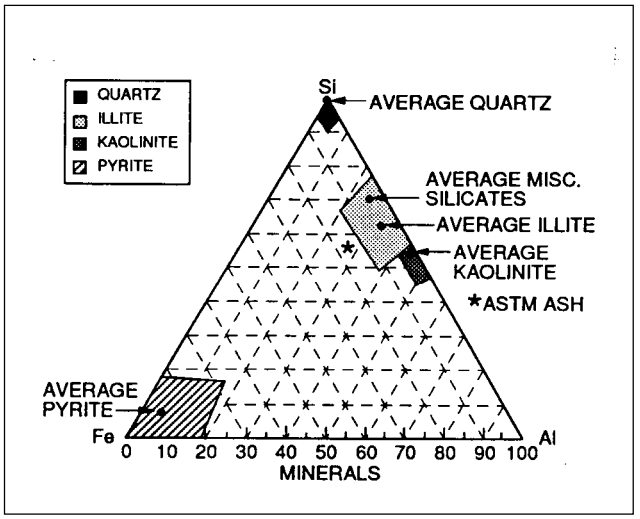

Figure 6. Si-Al-Fe ternary diagram showing typical composition ranges from minerals in coal. Reproduced by permission of Engineering Foundation.[111]

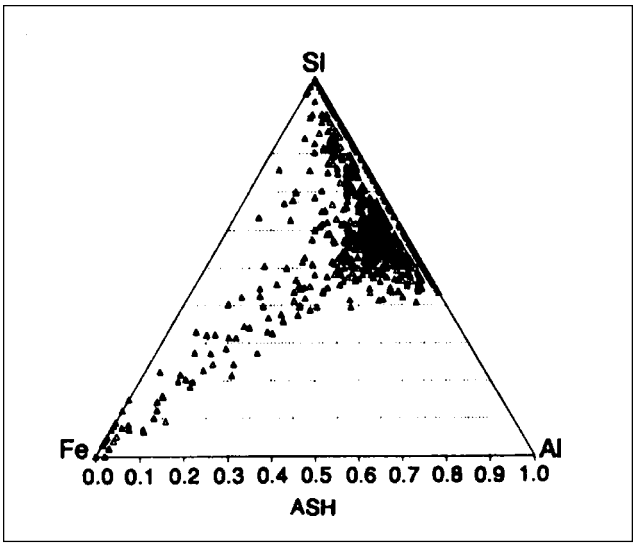

Figure 7. Measured elemental compositions in individual coal fly ash particles. Reproduced by permission of Engineering Foundation.[111]

While complex models have been developed to predict fragmentation behavior,[113,121–124] validation of these models has been limited, and complicating factors such as adhesive forces have been neglected in past analyses.[125] The models provide useful qualitative information but cannot predict quantitative trends with confidence. The fragmentation scales with the ratio of the volume fraction of ash in the char to the void fraction, Λ.[122] For high values of Λ, fragmentation is negligible, and one ash particle is produced per coal particle. For low values of Λ, extensive fragmentation occurs, and each mineral inclusion produces a separate ash particle. These trends are well illustrated by the results of Wu et al., who showed that as pressure increases during pulverized coal combustion, the macroporosity increases and the ash produced becomes finer.[126]

The particle-to-particle variation in particle density is an added complication. Figure 7 shows that a typical ash sample is a mixture of particle compositions. A number of the ash particles have high iron content and may be expected to have densities more than twice that of the aluminosilicate-rich particles. In addition, a large number of the particles will form cenospheres (hollow spheres) or plerospheres (hollow sphere surrounding a number of spherical ash particles).[83,112,127,128] The mechanism for the cenosphere is the formation of gas within the ash particle in a temperature window where the viscosity is low enough to favor the bubble growth but not so low as to have the gas escape and the bubble collapse. One mechanism for cenosphere formation identified by Raask[128] is the reaction within the ash of iron oxide with carbon to form CO. The cenospheres can grow to sizes up to 300 μm. Up to 5% of the fly ash has been observed to form cenospheres having a specific gravity less than 1.0.[112,128] If a 50-μm particle with

a specific gravity of 2.5 formed a cenosphere with an outer diameter of 100 μm, the wall thickness would be ~2 μm and the specific gravity of the particle would be 0.625. The wall thickness decreases with the square of the diameter of the cenosphere and therefore will be submicrometer for the largest cenospheres (>300-μm diameter). Indeed, it has been postulated[83] that one source of the submicrometer particles is provided by the fragments of cenosphere shells.

It can be seen that the multimodal distribution of combustion particles is governed by a number of factors. The submicrometer fraction is generated by the vaporization and condensation of particles and, to a lesser extent, the fragmentation of cenospheres. The supermicrometer particle size distribution is governed by the size distribution of the coal, the mineral matter distribution within each size fraction, the fragmentation of the char during combustion, and the formation of cenospheres. Although the processes governing the size distribution of fly ash are well understood qualitatively, they are sometimes difficult to quantify, most particularly the char fragmentation during combustion. The simple models of one ash particle per mineral inclusion and one ash particle per coal particle provide limiting solutions for the impact of fragmentation. A comparison of experimental data with these limiting solutions is shown in Figure 8 for one case. Because of the importance of fly ash as an additive for concrete manufacture, there are extensive compilations of fly ash size distribution and composition.[129,130]

Special Considerations for Large and Small Particles

Combustion particle diameters range from nanometers to millimeters, a size range which represents a mass range of a factor of 10^{18}. Special considerations are needed for both size extremes. The behavior of the largest particles is dominated by gravity settling, and they are usually considered as bottom ash rather than as aerosols, but this is an arbitrary distinction from a particle formation standpoint. Most reported measurements of combustion particles from coal, biomass, and even from oil are truncated at the upper end by the cutoff of the sampling apparatus. While these macroscopic particles are of no concern for inhalation toxicology, they are important for closing mass balances in both laboratory and full-scale measurements.

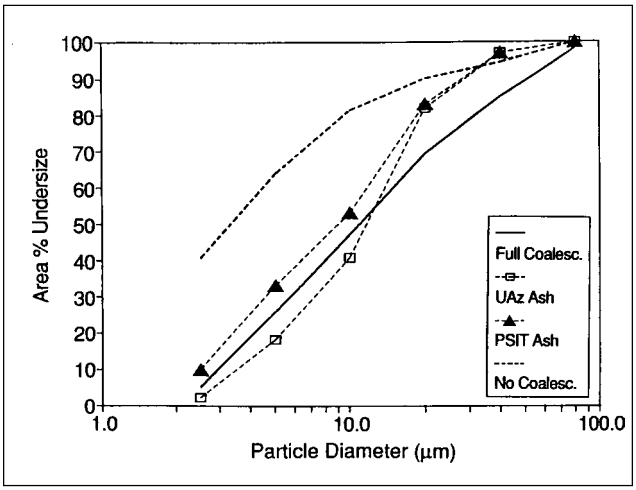

Figure 8. Ash particle size distributions (PSDs), model (solid and heavy dashed line) vs. experiment (symbols) for Upper Freeport coal. Reproduced by permission of Engineering Foundation.[111]

The fume formed by nucleation and condensation of vaporized ash, ash, and organic materials is typically a combination of true nuclei, a transient mode of nuclei that have undergone coagulation and surface growth, and accumulation-mode particles, depending on the relationship between the characteristic time for coagulation and the age of the aerosol when it arrives at the sizing instrument. Combustion particle number size distributions often show a truncated curve with the number of particles in each size range still increasing as the small size limit of the instrument is reached. This suggests a pool of particles exists below the 5–10 nm cutoff[131] of most current particle-size instruments.

Recently, the existence of high concentrations of 1–2 nm combustion particles has been reported.[132,133] These particles cannot be detected by most instruments used for studying submicron aerosols, but can be detected by light scattering and absorption in the near UV. They have a longer life span than would be expected from the coagulation rates discussed above. In the conventional coagulation models, the assumption is made that the sticking coefficient is unity; that is, every collision results in coalescence or aggregation. This is a reasonable assumption for accumulation mode particles; however, nuclei particles on the order of 1–2 nm may have lower sticking coefficients, as was shown by Narsimhan and Ruckenstein in a theoretical study of equal-sized neutral particles that considered the competing effects of van der Waals attraction and Born repulsion.[134]

Acid Aerosols

H_2SO_4 may be considered as either a gas-phase or particle emission depending on the sampling method. Some portion of the total sulfur in the fuel is converted to SO_3 and forms H_2SO_4 in the presence of water in the hot combustion products. The dew point of H_2SO_4 in the undiluted combustion products from fossil fuels is much higher than ambient temperature, and the acid may nucleate and condense to form aerosol particles as the gas is diluted and cooled, either in the unconfined stack plume or in a dilution sampler. Filter-based particle mass measurement methods in which the undiluted gas is

passed through a heated sample train can result in the acid remaining in the gas phase. On-line particle number measurements typically require diluting the stack gas to bring the concentration within the range of the instrument, and this results in the acid being measured as PM.

The amount of acid aerosol formed depends on the partitioning of sulfur between SO_2 and SO_3 and on the temperature and humidity of the dilutant gas. The formation of SO_3 is kinetically limited and can be enhanced by catalytic reactions with metals in coal combustion ash[135] or in catalytic NO_x reduction equipment. Typical acid dew points for coal combustion are 380–395 K.[136] For aircraft engines at cruise altitude, the SO_3 measurements are much higher than expected based on hydroxyl and atomic oxygen reaction rates, suggesting another, possibly heterogeneous, pathway.[137] The influence of dilution conditions on aerosol formation are discussed in the measurements section.

Particle Shrinkage by Evaporation and Oxidation

Unlike inorganic oxide particles, which are stable under post-combustion conditions, both condensable aerosol and soot mass can decrease after particles are formed. The organic aerosol, H_2SO_4 aerosol, and hydrated species can evaporate at rates that are well described by local phase equilibrium and diffusion mass transfer rate equations. Soot is destroyed in the flame by oxidation, and soot emissions are much lower than the initial soot volume fraction that occurs in the fuel-rich zones. The rate of soot oxidation can be estimated from the semiempirical kinetic formula proposed by Nagle and Strickland-Constable.[138] However, this correlation overstates soot oxidation at temperatures below 1800 K[34] and understates the oxidation rate in low-oxygen conditions where OH radicals are important.[33] The fractal aggregate structure typical of soot particles further complicates soot oxidation estimates because simple spherically symmetric mass diffusion equations are a poor approximation.

CONTROL DEVICES

The particles emitted from the stack will have a size and composition distribution very different from that in the combustion system because of the size-dependent collection efficiency of any APCD equipment. Historically, the combustion and atmospheric emission research communities have been uncoupled. Combustion researchers generally concentrate on the particulate formation in the flame zone of laboratory and pilot-scale equipment, since this allows close control of experimental conditions. Most field emission studies focus on measurements in the stack, since stack PM is of regulatory concern. Measurements of uncontrolled emissions at the exit of an industrial-scale combustion chamber are difficult and expensive, so data are seldom collected. The particle emission mass measured downstream of modern, high-efficiency particle-removal equipment largely reflects variations in gas-cleaning efficiency, not changes in combustion conditions. However, some details of the primary combustion particles, such as particle morphology and elemental concentration within an aerodynamic size range, are preserved from the combustion chamber to the stack. A few researchers have studied the particles upstream and downstream of the APCD. For example, Itkonen and Jantunen present graphs of elemental size distribution upstream and downstream of the ESP from a plant that co-fired peat and oil.[139] These studies provide an important link between particle formation in combustion and human health impacts.

Gas-cleaning equipment for particle removal includes cyclones, fabric filters, ESPs, and scrubbers on stationary furnaces. Internal combustion engines are equipped with catalytic converters, and particle traps are coming into commercial use on diesels. Particle removal requires some combination of inertial separation, which becomes more efficient with increasing particle size, and diffusion to a solid or liquid collection surface, which becomes more efficient with decreasing particle size. The result is that the removal efficiency of particles from air is least efficient in an intermediate size range from 0.1 to 1 μm. This minimum PM removal efficiency is observed in post-combustion cleanup equipment at the source, in the atmosphere, and in the respiratory system. The fundamental physics of these particle removal processes are covered in aerosol texts,[51] and the related equipment design and performance equations are covered in air pollution control handbooks.[140–142] The stack emissions of specific combustion particle types depends on both concentration of particles in each size range at the combustion chamber exit and on the size-dependent collection efficiency in the gas-cleaning equipment. Understanding the particle size and composition at the source allows developing computational models that can predict practical information such as the penetration of each trace element through an ESP installed on a coal-fired power plant.[143]

The collection efficiencies of three types of particle collectors are shown in Figure 9.[144] The minimum efficiency for all three devices is in the range between the regimes of deposition by inertial and diffusional processes. For a given technology, the actual efficiencies will, of course, vary widely with changes in design and operational parameters. A measure of the wide variation in the penetration of particles through operating ESPs at power plants is provided by Helble[143] and summarized in Figure 10. Again, the peak penetration occurs in the 0.1- to 1-μm size range, where the particle size is comparable to the mean free path of the gas. The collection efficiency of the

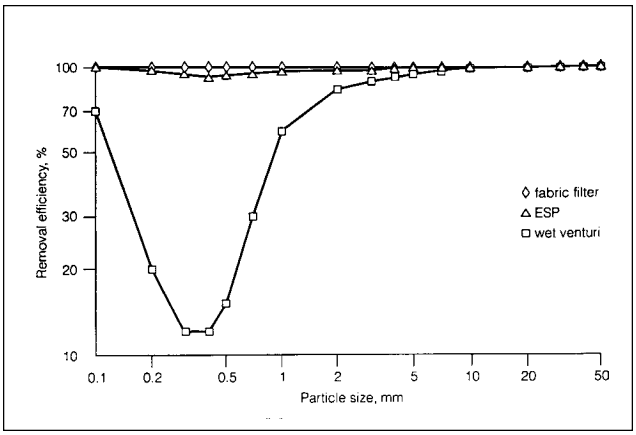

Figure 9. Removal efficiency of three common particle removal technologies used on large stationary combustion systems. Reproduced by permission of IEA.[144]

smallest particles by an ESP is reduced because a portion of the incoming ultrafine particles do not receive a charge (partial charging).[145–147] However, in the ultrafine size range, diffusion and particle growth by condensation of water vapor become important removal mechanisms.

Since the collection efficiency of a particle control device is size-dependent, the varying partitioning of elements between the submicron particles, residual fly ash, and vapor will lead to a wide range of elemental collection efficiencies that will differ from the overall PM collection. Kauppinen and Pakkanen reported the emissions of 17 elements by particle size based on measurements in the stack of a coal-fired power plant equipped with an ESP.[148] Three elements are shown in Figure 11. Aluminum is found in the supermicron particles, while sulfur is found in particles smaller than 0.1 μm. Cadmium shows a bimodal distribution.

Extensive data have been obtained by EPRI and the U.S. Department of Energy (DOE) on the collection efficiencies of coal-fired utility boilers for the elements regulated under the Air Toxics provision of the Clean Air Act

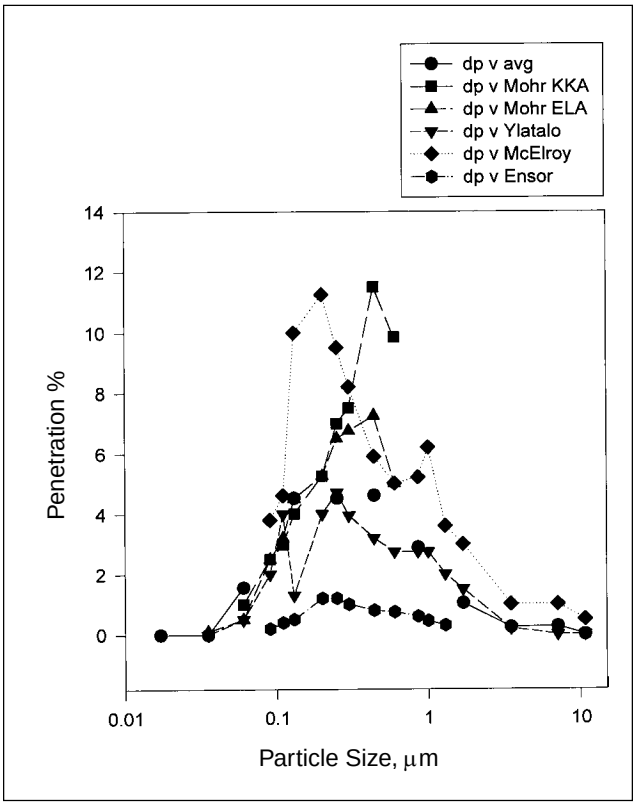

Figure 10. Summary of studies reporting penetration of coal fly ash through an ESP. Reproduced by permission of Elsevier Science.[143]

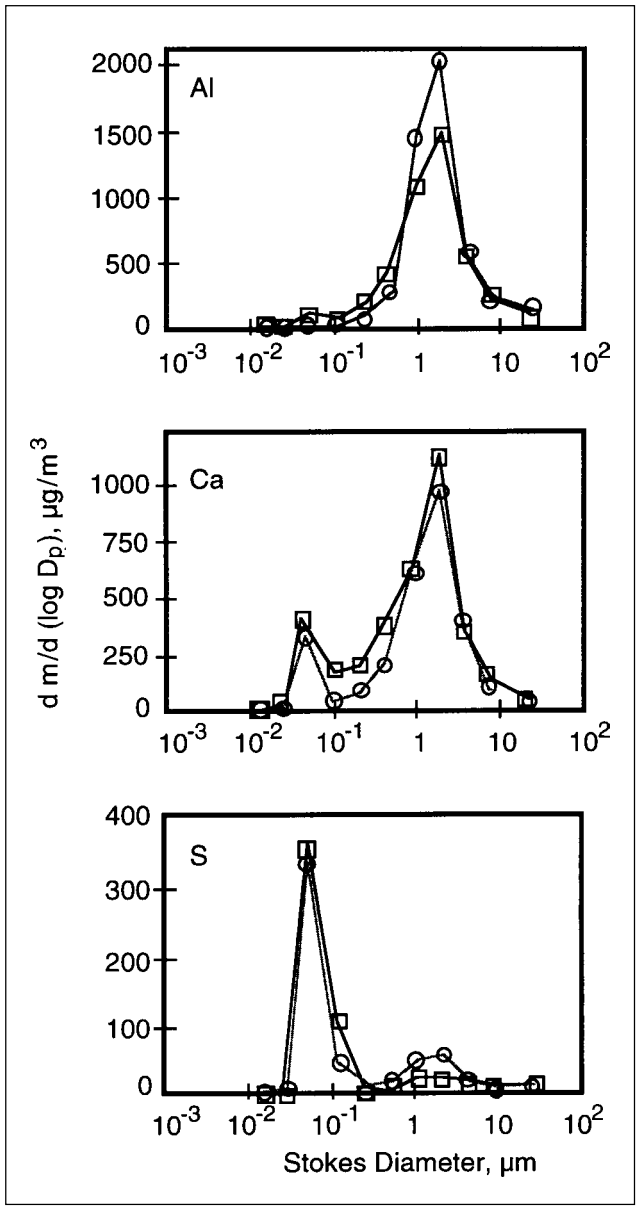

Figure 11. Distribution of selected elements by particle size as measured in the stack of a power plant equipped with an ESP. Some elements, such as Al, are concentrated in the large particles, while others, such as S, are concentrated in the submicron particles. Some elements show a bimodal size distribution. Replotted from more complete data presented by Kauppinen and Pakkanen.[148]

Amendments.[149–151] These data will be used to illustrate the relationship between combustion emissions and stack emissions. The data on the collection efficiencies of particles and elements in ESPs compiled by Helble[143] is summarized in Table 2. The collection efficiency for some elements approaches the overall particle collection efficiency. Elements enriched in the fine particles have a slightly lower collection efficiency. Metals with high vapor pressure, Hg and Se, have a much lower collection efficiency across the ESP than the total particle removal. A wet scrubber for SO_2 removal also selectively removes species adsorbed on particles and can cause chemical reactions on the particles by humidification at moderate temperature and entrainment of chemicals from the sorbent solution.[152] Additional aqueous-phase and photochemical reactions can take place in the stack plume and atmosphere.

Correlations between the emissions of elements from a boiler with the mass of elements fed with the coal[150] do not provide any insights on the effect of combustion conditions on the emissions. It is desirable to develop models to determine how the emissions are influenced by changes in combustion operating and design parameters. Laboratory studies have provided the mechanism for vaporization and condensation processes that govern the size and composition of the ash that can be used to develop ash transformation models. To be able to determine the effect of changing combustion modifications or changing APCD performance, one needs to combine a size-dependent model of emissions with a size-dependent model of APCD performance. Such a model has been developed by Helble in his retrospective analysis of the EPRI and DOE field studies of air toxics emissions.[143] For the fundamental combustion particle studies to be useful to the regulatory and health communities, more attention needs to be paid to the role of the downstream heat transfer sections, the APCD, and the initial plume condensation in modifying composition and size distribution of the emissions from the combustor. Until suitable integrated computational models of the downstream processes are available, the best measures of the contribution to human exposure from various combustion sources will be empirical data from stack or exhaust measurements.

Table 2. Field data on trace element capture efficiencies in ESP.

Element	ESP Capture Efficiency	Metal Capture/ Particle Capture
Vapor-Phase Metals		
Hg	28.9%	0.29
Se	49.1%	0.49
Fine-Particle Enriched		
As	96.1%	0.969
Pb	96.8%	0.976
Not Enriched in Fine PM		
Co	98.2%	0.992
Mn	98.5%	0.993

Note: Elemental capture in the ESP depends on the size-dependent partitioning of the metal to particles. Data from Helble.[143]

A summary of the emissions from these four different combustion applications follows. It should be noted that there is wide variability in both the source PM and in the downstream particle removal efficiency depending on fuel type and combustor size. Coal-fired boilers are equipped with high-efficiency APCD and emit particles enriched in the 0.1–1 μm range, where the particle removal efficiency is at a minimum. Oil-fired boilers often do not have any APCD because of the low ash and sulfur content of the fuel. As a consequence, large particles, such as coked fuel residue, may be emitted in addition to the submicron condensation aerosols. Small combustors, such as fireplaces and open burning, do not have any particle control devices.

SPECIFIC COMBUSTION APPLICATIONS

This section discusses the particle emissions entering the atmosphere from various practical combustion applications, both with and without post-combustion particle removal and gas cleaning. Typical data on PM mass emissions, size distribution, and composition are provided for convenient reference. The citations can serve as a starting point for a literature search, but a comprehensive review of the literature for each of these individual applications is not attempted. The extensive compilation of combustion emission factors prepared by the EPA[153] emphasizes PM_{10} mass and provides little data on particle number distribution or on chemical composition of the PM.

Residential and Commercial Boilers and Furnaces

Distillate fuels, generally kerosene and No. 2 fuel oil, are widely used for domestic and process heat in areas where natural gas is unavailable. Direct population exposure to oil combustion emissions occurs because the fuel is burned in populated areas, and the furnaces do not have post-combustion particulate controls. The PM is mainly sulfate aerosol from fuel sulfur and soot plus organic aerosol from incomplete combustion. The ash content of distillate fuel is small, but not zero, so the emissions also contain inorganic components. In a study of homes with and without kerosene space heaters, the kerosene heaters were estimated to add ~40 $\mu g/m^3$ of total $PM_{2.5}$ and 15 $\mu g/m^3$ of SO_4^{2-} to the indoor air.[154] Hildemann reported that the emission factor for particles smaller than 0.7 μm from an industrial-scale boiler fired with No. 2 fuel oil was 8 μg/kJ

of fuel.[155] These boiler emissions contained a mode near 50 nm and a larger mode near 0.5 μm. The fine particles consisted of about 32% sulfates, 29% EC, 6% organics, 6% NH_4^+, and 3% other ionic and oxidized trace species (mainly SiO_2, Al_2O_3, Fe_2O_3 and Na^+).[156] The balance of the mass was in unidentified substances and may have included water in the form of hydrolyzed compounds. Detailed composition of the organic carbon (OC) portion of oil-boiler PM was also reported.[157]

Residual Oil Fly Ash

Residual fuel oil is a highly viscous product that has a much higher ash content than distillate fuels, since the metals in the crude oil, as well as contamination from refinery catalysts and equipment, are concentrated in this fraction. Residual fuel oil is burned in some power plants, for example, in the eastern United States. Similar heavy fuel oil grades, Bunker C and marine diesel, are burned on ships, and these emissions are suspected to have a significant air quality impact on coastal cities. Metal mobilization from residual oil fly ash has been extensively studied[158–160] because of the high content of V and Ni, which is different than other combustion PM.

The emissions from residual oil are multimodal, with a mode centered at 70–80 nm, but with most of the mass in a residual ash mode composed of cenospheric carbon-rich particles extending beyond 100 μm in diameter. Carbonaceous material can be greater than 75% of the mass emissions from small residual oil-fired boilers.[161] The formation of carbonaceous PM during residual oil combustion is related to the asphaltene content of the fuel.[162,163] When the residual oil is burned more efficiently under conditions typical of a utility boiler, the carbon content is lower and the PM is almost entirely in the ultrafine (condensation) mode.[164] The transition metals in residual oil combustion ash are in the form of sulfates rather than sulfides or oxides.[165–167]

Coal-Fired Steam Generation Boilers

The stack emissions from coal-fired utility boilers are affected by the particle generation during combustion and by particle transformations and size-selective removal during cool-down and gas cleaning. Power plant coal combustion including pollutant formation,[168,169] ash formation and deposition,[115] submicron particle formation,[14,66,170] and metal transformation[73] have been reviewed. The inorganic particle stack emissions consist of a supermicron mode containing spheres of mineral ash and a submicron mode formed by mineral vaporization and condensation, as discussed above. The carbonaceous emissions consist of supermicron char particles remaining from incomplete combustion of the parent coal. Submicron carbon-rich particles, suggestive of soot, are also present in the exhaust from both laboratory- and full-scale coal combustors.[171–174] Figure 12 shows the cumulative mass emissions versus size for a sample of power plants including both pulverized coal and cyclone burners.[118,175,176] The multimodal size distribution of the emitted PM is indicated by the changes in slope of the cumulative mass curve. Full-scale data show that an ultrafine particle mode can be detected for both circulating and bubbling fluidized bed coal combustion, but the ultrafine concentration is several orders of magnitude smaller than the ultrafine PM concentration produced by pulverized coal combustion.[177,178]

Many of the field studies of coal-fired power plants were aimed at obtaining the information needed for regulatory purposes, so the measurements have focused on the total mass of the emissions. Selected field studies have determined the fractions of the trace elements entering a boiler that enter the flue gases and pass out of the unit through the stack.[63,78,88,148,152,179,180] Additional efforts have focused on the effectiveness of APCDs in removing these potentially toxic substances.[63,78,179,180] These studies provide the following information:

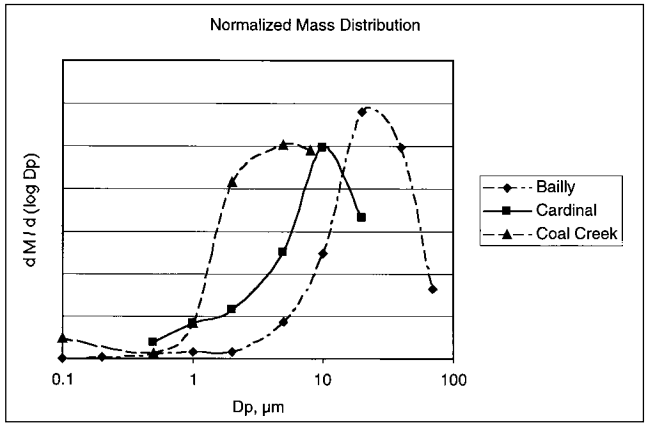

Figure 12. Normalized differential particle mass distributions measured in the stack for a sample of coal-fired power plants using different burner and gas-cleaning technologies. Data compiled from DOE field studies in 1993–1994.[118,175,176] The stack particle mass emission rates vary between replicate runs by about a factor of 2 due to sensitivity to plant operating conditions.

Plant	Description	Stack Emissions
Bailly	345 MW, Cyclone Burner Dry scrubber, ESP Illinois high-sulfur bituminous	60 kg/hr
Cardinal	615 MW, well-mounted cell burner ESP, no sulfur removal Pittsburgh No. 8 bituminous	100 kg/hr
Coal Creek	550 MW, tangential-fired Wet scrubber, ESP North Dakota lignite	260 kg/hr

- The inorganic ash size distribution is multimodal. The submicrometer particles consist of aggregates of primary particles that have grown to 10–50 nm. The larger particles consist of spherical particles, including cenospheres and plerospheres.[120,127,181]
- Particles entering the APCD are essentially bimodal in terms of mass, with on the order of 1% of the ash consisting of submicrometer particles and the larger residual ash falling into the 1–20 μm range.[54,63,180,182]
- Particles in the 0.1–0.3 μm range have the highest penetration through APCD compared with both larger and smaller particles,[63,78,179,180] so the 0.1–1 μm particles form a larger fraction of the mass distribution leaving the APCD than they do in the uncontrolled combustion emissions.[63]
- The submicrometer ash is enriched in volatile elements relative to the larger particles.[148,152] The concentration of the trace elements within the submicrometer and supramicrometer ash fraction increases with decreasing particle size.[73,88]
- The surfaces of the ash particles are also enriched in volatile elements relative to their core.[88]
- The major influence on the fraction of ash that is vaporized is the temperature.

Because NO_x is also temperature-dependent, a correlation between high NO_x emissions and high amounts of submicron particles has been reported[55,64,76] for boilers in which the thermal (Zeldovich) kinetics dominate the NO_x emissions. For modern, post-New Source Performance Standards boilers, the NO_x emission is dominated by fuel nitrogen. The correlation between NO_x and submicron particle formation is not as well established for these conditions, since conversion of fuel nitrogen to NO_x is controlled by staging the air, and NO_x formation does not necessarily correlate with temperature.[183–185]

Metals may partition into three major emission streams: the stack, the bottom ash, and the fly ash collected during gas cleaning. An example of this type of data, summarized in Table 3, shows the points in the power plant process where As, Cr, Hg, and Se are removed and the fraction of that element in the raw coal that is emitted from the stack.[186] The toxic metals in the PM emissions are the result of fuel composition, combustion conditions, and downstream cleanup. Coal washing can greatly reduce the input of toxic metals to the boiler. A small fraction of the volatile metals is removed with the bottom ash, some metals are adsorbed on particles and removed in the ESP, and flue gas desulfurization systems can remove metal ultrafines and vapors. Metal emissions from coal-fired steam generation boilers are not currently regulated in the United States. Table 4 lists typical physical characteristics and chemical composition of coal fly ash.[129,130,187–189] Coal fly ash typically contains less than 5% unburned carbon, but problems with char burnout can result in much higher carbon values.[125,190–192]

Elemental balances on power plants show that ~1–4% of most metals in the fuel are emitted in the stack PM.[143,148,152,178,193] The major exceptions are Se and Hg, which escape as vapors. Rapid quenching from high temperature results in the formation of glass-phase species of indeterminate composition rather than the crystalline minerals with similar elemental composition. Optical microscopy on fly ash from ESPs shows that 11–48% of the fly ash has crystallized at the cooling rate normally encountered in boilers. Iron in an alumino-silicate glass is a characteristic phase found in coal fly ash formed under both oxidizing and reducing conditions.[194–196] The presence of large concentrations of alkali and alkali earth elements, typical of western U.S. coals, enhances glass formation and decreases crystallization.[129]

Table 3. Elemental partitioning in a coal-fired power plant.

	Coal Washing	Boiler Bottom Ash	ESP or Fabric Filter	Flue Gas Desulfurization	Emitted from Stack
As	65–75	0–2	85–99	0–20	0–5
Cr	30–75	3–20	85–99	0–20	0–2
Hg	30–40	0	0–60	10–90	5–95
Se	25–50	0–5	10–80	0–50	20–80

Note: Data obtained during the DOE PISCES program shows the percent of the element in the raw coal that is removed at various points in the process. Based on original DOE report and other reports.[186]

Large-Scale Biomass Combustion

Concerns regarding trade balance, global warming, and disposal of agricultural residue have led to an increased interest in biomass as a renewable energy source. The unique characteristic of biomass PM is the high alkali content, especially K,[197,198] compared to fossil fuel combustion ash. Studies have been conducted of industrial-scale biomass combustion, especially in fluidized bed boilers.[199,200]

The ash formation processes during suspension firing of wood sawdust and sanderdust have been shown to be similar to the mechanism for pulverized coal combustion,[201] as indicated in Figure 3. The supermicron particles are predominantly Ca, but also contain Fe, Al, Mn, and Si. The alkali minerals form a submicron condensation aerosol that is ~30% of the total ash mass, which is much higher than the fraction of submicron ash from coal combustion.

Cofiring of crop residues with coal in existing power plants has been proposed as an

Table 4. Typical coal fly ash properties.

	Typical Value	Range	Notes
Specific Gravity (single particle)	2.2	1.8–2.6	<1 for cenospheres
Specific Gravity (bulk ash)		1.1–1.5	includes voids between particles
Elemental Composition	**Typical %**	**Range %**	**Expressed as Oxides**
Al_2O_3	25	13–36	
SiO_2	45	22–61	
Fe_2O_3	20	4–20	
CaO	2.6	1–22	
MgO	1.3	1–5	
TiO_2	1.2	1–3	
Na_2O	0	0–8	
K_2O	2.1	0.3–4	
SO_3	2	0–25	
Trace Metals		ppm levels	
Phase Distribution	**Typical %**	**Range %**	
Unburned Carbon	3	0 to >10	
Amorphous Glass		50–90	
Crystalline Minerals		11–48	
Major Minerals		**Range %**	
Mullite		2–20	$Al_6Si_2O_{13}$
Quartz			SiO_2
Iron Spinel			$(Mg,Fe)(Fe,Al)_2O_4$
Hematite			Fe_2O_3
Anhydrite			$CaSO_4$

Notes: Typical fly ash composition is for Pittsburgh No. 8 high volatile bituminous coal fly ash; ranges compiled from various sources.[129,187,188]

economical way to reduce PM emissions from open burning in the fields and to replace fossil fuel.[202] Laboratory studies of inorganic species behavior during cofiring have been conducted.[203] A field study of cofiring coal and straw reported a number concentration of 5×10^7 particles/cm^3.[204] This high number concentration may be due to the use of an injector diluter installed directly in the flue.

Domestic Combustion

A significant amount of combustion takes place indoors, for example, tobacco smoking, natural gas appliances, oil-fired furnaces, fireplaces, and wood stoves. Domestic combustion is especially important when considering population exposure to combustion particles on a global basis. Smoke from small-scale domestic combustion of biomass, locally produced coal, and other opportunity fuels results in a direct exposure to sensitive individuals, such as the elderly and children, since the fires are located in or near homes. Fresh and aged wood smoke may be especially important for health effects because the small particle size results in enhanced deposition in the lower respiratory tract.[205] Cooking and heating with biomass represents a large portion of the total combustion in developing economies. For example, household biomass combustion in Pakistan is estimated to represent 37% of the total primary energy consumption of the country.[206]

Poorly ventilated cooking fires can create indoor particle levels that are far above the U.S. ambient PM standard of 150 $\mu g/m^3$. A geometric mean kitchen PM_{10} concentration of 1830 $\mu g/m^3$ was reported in a study of Bolivian highland villages.[207] The kitchen $PM_{2.5}$ concentration in homes using biomass for cooking averaged 555 $\mu g/m^3$ with a maximum of 1493 $\mu g/m^3$ (n = 7 homes) in rural Mexico.[208] Recreational biomass fires are a surprisingly large source of combustion emissions in developed countries, and fireplace restrictions have been imposed in many cities and mountain resort communities to avoid violations of the current PM_{10} standard. For example, combustion of wood in residential fireplaces has been estimated to contribute 14% of the annual average OC emissions to the Los Angeles urban atmosphere.[209]

Particle emissions from biomass vary with both the combustion conditions and the fuel type. One study of PM emissions from residential wood fires distinguished between hot, rapid combustion and slower, low-temperature, air-starved combustion.[210] Hot burning produced a monomodal particle distribution with 30–40% of the particles between 0.3 and 0.6 μm. The particles were predominantly EC and OC, but contained percent levels of K, Cl, and S with 0.01–1% levels of Al, Si, P, Zn, Pb, and Fe. For cool burning, the particles were largely OC, and almost 50% of the carbon was associated with particles between 0.6 and 1.2 μm.

Combustion efficiency, wood moisture, and dilution gas temperature affect the particle size distribution, indicating that the actual winter fireplace PM may have a higher fraction of fine particles than are measured under laboratory conditions.[211] Hildemann provided detailed particle size distribution graphs of fireplace emissions and calculated an emission factor of 10 g PM/kg wood burned based on electrical aerosol analyzer size measurements, and reported 16 g/kg based on filter weight.[155] Rogge reported fine particle emissions from fireplaces ranging from 6.2 g/kg for oak to 13.0 ± 4.0 g/kg for softwood,[209] and suggested that unique organic species, such as tricyclic resin acids, can serve as markers of wood smoke in the

atmosphere. The amounts of various PAH compounds resulting from domestic combustion of biomass fuels have been reported.[209,212,213]

Regional differences in domestic combustion may provide the opportunity to conduct long-term exposure health studies that integrate epidemiologic methods with detailed characterization of the PM. For example, domestic combustion of coal has been associated with the high incidence of lung cancer in Xuan Wei, China.[214] Chemical characterization of indoor air in homes using smoky and smokeless coals showed 1–2 orders of magnitude differences in the concentration of PAH. The PAH and polar extracts from the particles in homes using smoky coal were highly mutagenic.[215–217]

Wildfire and Agricultural Burning

Open fires from wildland and agricultural burning are a significant source of atmospheric PM on a global scale. Concerns include acute health effects to people near the fires, climate effects,[218] and regional visibility.[219] PM from large fires can be transported over continental distances. High PM_{10} in the eastern United States during the summer of 1998 was caused by smoke from fires in Mexico,[220] as shown by satellite photos. EPA policy[221] does not consider exceedances of National Ambient Air Quality Standards (NAAQS) from natural events such as seismic and volcanic activity, wildland fires, and high wind to constitute a violation for the legal purpose of designating non-attainment areas. However, high particle concentrations are a health and environmental concern whether the source is classified as natural or anthropogenic. Fire is important for recycling nutrients and for preventing the spread of invasive species in many ecosystems. Balancing the ecological role of fire with the goal of minimizing particulate levels in populated areas is a concern for land management in the western United States and in other areas with grassland ecosystems.

Emissions from wildland and agricultural fires are poorly characterized because of the variability in combustion conditions, for example, upwind versus downwind propagation, fuel loading per area, and fuel moisture. Hot fires produce more NO_x, but less CO, unburned hydrocarbons, and soot than smoldering fires. Quantitative data on particle size, number concentration, and chemical composition that would be useful for epidemiology correlations and for mechanistic toxicology studies are limited by the difficulty of field measurements and the uncertainty of how to scale from laboratory experiments to real open fires. Inventory estimates of PM emissions from open fires are based on empirical factors for PM per weight of fuel burned multiplied by an ecosystem-based estimate of fuel loading per area. Typical emissions factors are: 4 g of total suspended PM/kg of biomass burned for piled logging slash with no soil debris; 16 g/kg for smoldering combustion of conifers in temperate forests;[153] and 20 g/kg for tropical forest fires.[222] Emissions of PAH have been measured in a wind tunnel for simulated open burning of cereal grasses and tree prunings.[223,224] Weakly spreading fires were observed to produce higher levels of the heavier PAH with more of the PAH partitioned to the particulate phase. PAH emissions were more strongly influenced by the burning conditions than by the type of fuel.

Oil Pool Fires

Management of large oil spills presents another case of balancing ecosystem health and ambient air quality standards for PM. Igniting an offshore oil spill can reduce the impact on aquatic and shoreline species, but also creates a large plume of particulate air pollution. An understanding of the characteristics of the PM emissions, as well as an understanding of the atmospheric dispersion and clearance, are needed to assess when to burn. Limited data on pool fire emissions are available from laboratory and mesoscale measurements.[225] The PM mass emissions range from 5% of fuel burned (50 g/kg) for laboratory fires to 15% of the fuel for a 17.2 m pool fire, showing that the smoke yield increases with increasing fire size. The particle size distribution from one mesoscale measurement was 50% of the mass in particles less than 0.7 μm and 90% in those less than 20 μm.[226] This is much larger than typical soot emissions, suggesting that the high particle loading in pool fire plumes allows large aggregates to form. The size of the primary particles that form the smoke aggregates increases with increasing fire diameter.[98,227] The primary particle size trends and morphology determined by thermophoretic sampling[228] for TEM examination are consistent with formation of soot on the fuel-rich side of the flame and agglomeration upon local flame interface extinction. Oil pool fire smoke is greater than 90% EC, and the PAH emissions from oil pool fires on water have been measured.[229]

Incineration Emissions

Much research has been done on metal transformations during hazardous waste incineration due to the controversial nature of the projects, and due to regulations that require quantifying metal emissions of incinerators during the permit application process prior to facility construction. Although incineration is a small source of PM emissions on a global scale, the unusual compositions of the waste feeds provide valuable insights into the thermochemistry of trace metals. For incinerators, the ash vaporization is affected by both temperature and Cl concentration, since the chlorides of many metals have a high

vapor pressure.[59,230] The formation of submicron particles and the formation of a bimodal particle size distribution in incinerators is very similar to the process that has been observed for coal. Unusual waste streams may result in incineration fly ash containing high levels of volatile metals, but in many cases the bulk of the particle mass from incinerator combustion is the refractory oxides.

An extensive review has been conducted by Linak and Wendt,[59] and Lighty and Veranth[231] have also discussed the issue. The partitioning of a metal in a hazardous waste incinerator depends not only on the temperature[59] and the gas environment, but also on the constituents within the solid matrix.[232] The metals either react with the solid matrix to form solid materials that might be nonleachable, or they may vaporize and undergo nucleation and particle growth similar to the processes previously discussed for submicron inorganic ash from coal. Vaporization also depends upon the type of metal. Normally, Cd[233] is found to be more volatile than Cr; however, the results depend on the solid matrix. The high levels of Cl present in incineration gas-phase emissions compared with fossil-fuel combustion affect the formation of fine PM.[230,234,235] The metal chlorides are generally more volatile than the metal oxides, so Cl causes higher vaporization, which leads to increased formation of submicron particles enriched in trace elements. Differences have been observed between the effect on particle size of inorganic versus organic Cl, that is, NaCl and PVC in the feed,[236] suggesting the importance of intermediate species in the reaction pathway.

If a listed toxic metal remains with the solid, the ash must meet land-disposal regulations, which require a leachability test. Research has shown that Pb may interact with the aluminosilicates in solid materials.[59,237,238] Others have studied the injection of sorbents for metals control, which captures the volatile metals in a sorbent-derived particle.[102,232,239,240] In some cases, a non-leachable solid was formed.

Laboratory-scale elemental composition and particle size data have been reported for conditions applicable to commercial incinerators.[241] Metal speciation data is more difficult to find since the metals are normally present only in trace amounts, which are difficult to detect by many speciation methods. However, Linak et al. demonstrated that the toxic form of chromium, Cr VI, was only a few percent of the total chrome emitted from a laboratory scale system,[242] except in the presence of Cl. When large amounts of Cl were present, the percent emitted was between 5 and 8%, still low. Thermodynamic calculations also show that input waste composition has a greater effect on Cr VI formation than does operating temperature.[243]

Data on full-scale incinerators are collected at the stack to demonstrate compliance with emissions limits. Due to the high particle removal efficiency, the emissions from incinerators are controlled by gas cleaning equipment performance. Combustion conditions impact emissions indirectly through changes in the particle size distribution, which influences air pollution control equipment performance. A study to characterize the performance of various incinerator gas cleaning systems showed that the PM mass concentration, corrected to 7% oxygen, measured at the secondary combustion chamber exit was 5 ± 0.6 mg/m^3, while the concentration downstream of a baghouse and ionizing wet scrubber combination was 0.013 ± 0.009 mg/m^3.[244] The control efficiency for individual elements ranged from 95 to 99.995% removal between the gas cleaning inlet and the stack. The differences in removal efficiency between elements are expected to reflect differences in the partitioning of each element to different particle size fractions, and to the liquid and gas phases. Kauppinen and Pakkanen presented graphs showing the elemental distribution in the emissions from a hospital incinerator,[245] which shows that Pb and Cd are enriched in the submicron particles. The authors are unaware of similar published data on the detailed size distribution of combustion exhaust or stack PM from commercial hazardous waste incineration.

Internal Combustion Engines

IC engines represent 20–40% of the fossil energy combustion in developed countries, and contribute emissions that are concentrated in urban areas. Particulate emissions from engines have been extensively studied due to concerns over the smoke emitted by diesel engines, lead emissions prior to the phase-out of leaded gasoline, and health effects of ultrafine particles. The general process of particle formation as discussed in the fundamentals section is fully applicable to IC engines. However, understanding particle formation in the cylinder of a high-speed engine involves both the chemical kinetics which have been determined from experiments in idealized laboratory flames and the transient temperature and volume changes, fuel/air mixing, and heat transfer unique to in-cylinder conditions.

A large body of specialized literature on IC engines exists. Details of engine design,[246,247] combustion in the cylinder,[248–252] in-cylinder measurements,[253] the use of fuel formulation and additives for soot control,[254] PM from catalytic converters,[255] and the development of particle traps for diesel engines[256] are outside the scope of this paper, and the reader is referred to the cited reviews and collected papers.

The filterable particles from IC engines, including both soot and inorganic PM, are either individual submicron particles or are loosely bound aggregates formed from ultrafine primary particles, as discussed in the fundamentals section. Soot and organic PM result from incomplete combustion. The inorganic particles are derived from fuel

and lubricant additives, fuel contamination, engine wear, and ambient PM that passed through the air filter. Caution is needed when looking for data on the fraction of ambient PM attributed to IC engines, because non-combustion particles from resuspended road dust and from the wear of tires and brakes are listed under "mobile sources" in some emissions inventories.

Soot formation in IC engines has been studied due to regulation of the black smoke that can be emitted by diesel engines under heavy load, and due to the importance of soot on radiant heat transfer and flame structure. The topic of soot from internal combustion is covered in detail in books by Heywood[257] and Sher.[258] Empirical data show that diesel smoke emissions increase with load, but can be reduced by improved fuel-air mixing and by better control of fuel injection. Work by John Dec and colleagues[259] using laser sheet visualization has shown that, under typical diesel conditions, the initial premix phase of diesel combustion occurs in a fuel-rich vapor-fuel/air mixture (equivalence ratio of ~4) in the leading portion of the fuel jet, just downstream of the maximum liquid-fuel penetration. This vapor-fuel/air mixture is fairly uniform with a sharp well-defined boundary at the jet periphery.

The measurements show that as autoignition occurs, the fuel breaks down over the whole premixed, fuel-rich region almost simultaneously (i.e., within ~70 μsec), followed very quickly (less than 70 μsec) by PAH formation throughout this region. Then, ~140 μsec later, initial soot formation occurs with very small particles forming throughout large sections of this leading portion of the jet. Within an additional 70 μsec, the entire region is filled with small soot particles whose volume fraction is increasing rapidly. The actual emission from the cylinder to the exhaust manifold is the result of competition between soot formation and soot oxidation. Soot oxidation is reduced when the combustion process is prematurely quenched. This occurs when excessive injection of fuel results in the burning mixture contacting the cylinder walls.

Table 5 summarizes exhaust measurements of particle size and number concentration data from selected studies of diesel and gasoline engines.[27,260–266] The exhaust tailpipe data show that IC engines are a source of particles smaller than 100 nm at initial concentrations greater than 10^6/cm^3, which is consistent with measurements of ambient particle size distributions at various distances from urban highways.[267,268]

The sizes of diesel particulate emission can be approximated by a bimodal lognormal distribution.[262] The nanoparticles in the ultrafine transient mode of diesel engines represent only 0.1–1.5% of particle volume (mass) but 35–97% of the particle number.[262] Most of the PM mass is in a mode with a diameter between 0.01 and 0.1 μm. From the available studies, the relative importance of surface growth and coalescence in determining the particle size in this larger mode is unclear. Typical exhaust PM mass concentrations from well-maintained modern diesel engines are 15–30 mg/m^3.[262] With older engines, the PM mass is higher, the number of ultrafines is much lower, and a condensation or accumulation mode dominates the number distribution.[269] The high particle number of 1×10^9/cm^3 reported for a 1991 Cummins engine by Bagley et al.[260] has led to the speculation that the reduced particle mass emissions in the newer diesels has resulted in increased particle number. The hypothesis is that there are insufficient soot particles to provide surface for the condensation of the heavier organic or acid molecules, which therefore become supersaturated in the vapor phase and nucleate as the exhaust cools in the sampling train.[27]

Gasoline engines have much lower PM mass emissions than diesel engines. Tailpipe particle emission mass is as low as 0.1 mg/mi, and the baseline number concentration is 10^5–10^6 particles/cm^3,[264,266] which is consistent with the reported accumulation mode particle size. Graskow et al.[264] reported that the particle number from gasoline engines is highly unstable and that they observed intermittent spikes in particle number up to 2 orders of magnitude above the baseline. The formation of deposits in gasoline engines, which can contribute to particulate emission spikes, has been reviewed by Kalghatgi.[270] Fuel parameters have a strong effect on the fuel/air ratio at which the maximum gasoline engine particulate emissions occur.[271]

A single instrument cannot measure the entire range of inhalable particles from less than 10 nm to over 10 μm that are potentially emitted by an IC engine. By using both a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer, the full particle size distribution from an engine can be reported in segments. For a diesel engine, Morawska et al. reported 10^4–10^5/cm^3 in the accumulation mode centered on 0.1 μm and ~1 particle/cm^3 in the range from 1 to 10 μm.[263] One particle at 5-μm diameter weighs the same as 1.2×10^5 particles at 0.1-μm diameter. The uncertainty introduced by interconverting particle mass concentration and particle number concentration data for the purpose of testing health effects hypotheses related to vehicle emissions is apparent.

Mass and surface area of submicron particles are inferred from number and diameter measurements assuming a spherical shape and an appropriate density. Comparisons of filter samples and the total emission mass calculated from integrating particle size and number data agree semiquantitatively,[265] generally within a factor of 2. This difference may not be significant compared with the wide range of PM emissions from real vehicles depending on age, operating conditions, and maintenance history.

Table 5. Selected measurements of particle emissions from internal combustion engines.

DIESEL **Engine & Condition**	**Number Mean**	**Results**	**Reference**
1991 Cummins–various modes with and without catalyst	Nuclei 11–17 nm Accumulation 55–73 nm	>10E9 particles/cm^3. High number count in smallest size bin measured. Size distribution graphs and lognormal fit.	260
Newer catalyst-equipped, LNG-fueled, and older leaded-fuel vehicles	Count Median Diameter 39–60 nm	Exhaust number concentration, 1.5E4 for catalyst, 8.4E4 for LNG, 7.9E5 for leaded.	261
1995 direct injection–various modes	Nuclei 5–9 nm Accumulation 29–40 nm	1–7E7 particles/cm^3. High number count in smallest size bin measured. Size distribution graphs and lognormal fit. Mass 15–30 mg/m^3.	262
Various in-service engines 1983–1996	Accumulation 30–160 nm Also data on 0.3–30 μm size range.	0.7–3.9E7 particles/cm^3 in SMPS range. Particle number increased with increasing power.	263
Review paper	Nuclei 5–50 nm Accumulation 0.1–0.3 μm.	1E7–1E8 particles/cm^3. Graphs of particle number and size vs fuel/air ratio for various engines.	27
GASOLINE **Engine & Condition**	**Number Mean**	**Results**	**Gasoline**
1993 4-cylinder	Nuclei <10 nm Accumulation 70 nm	Emissions highly unstable. Baseline 1E5/cm^3 with spikes to 1E7/cm^3.	264
Review paper	40–70 nm	1E5–1E6 particles/cm^3. Varies with fuel/air ratio.	27
Various automobiles 1994–1997	30–70 nm	Did comparisons of total particle number and filter collected mass over test cycle.	265
Various automobiles 1995–1998	25–107 nm	Compared various results from test cycles. Mass 0.1–9.6 mg/mi.	266

A program of dynamometer tests on 23 in-service spark ignition vehicles ranging from 1976 to 1990 model years showed particulate emissions ranging from 7.2 to 1342 mg/mi,[272] and the OC ranged from 35 to 95% of the total carbon.

Various investigators have reported the chemical composition of IC engine PM as a function of particle size and operating conditions. The PM is a mixture of EC, organic compounds, metal oxides, and sulfates. The exhaust from a typical heavy-duty diesel is 31–41% EC or soot, 25–40% unburned oil, 7% unburned fuel, up to 14% SO_4^{2-} and H_2O, depending on fuel sulfur content, and 13% ash and other inorganic, and there is usually some mass listed under unknown origin.[27,273]

Data on partitioning between soot and the soluble organic fraction[274] and between EC and OC by thermal/optical reflectance from IC engine emissions are available.[272] Detailed organic composition of emissions from in-service gasoline and diesel engines by GC/MS analysis of extracts have also been reported.[272,275,276] As will be discussed in the measurements section, the H_2SO_4 and heavy organic products of incomplete combustion may form particles in the atmosphere that are not included in the PM as measured by standard procedures. In the United States, particulate emissions are regulated by the mass collected on a filter at 325 K (125 °F) followed by equilibration at 295 K and 45% relative humidity before weighing.[277] Figure 13 shows the complex nature of the condensable organic aerosol collected from diesel engines using a dilution sampler.[276] Only a small fraction of particle-bound material is resolved into known compounds, and even the resolved fraction contains multiple chemical compounds within each category. Dilution samplers[155,278] can quantify the mass and composition of the condensable

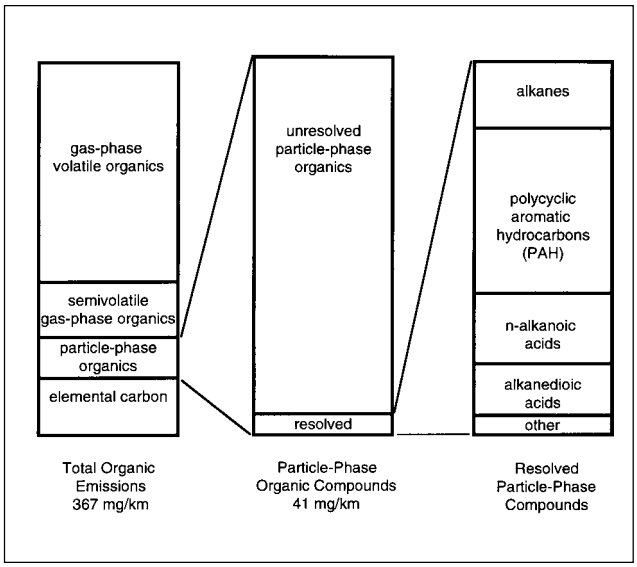

Figure 13. Organic analysis of the exhaust emissions from medium-duty diesel trucks. Only a small fraction of the particle-phase organics were resolved into identified compounds. Replotted from data by ref 276.

PM, but may distort the size distribution. The effects of dilution on PM size distribution will be discussed in the measurements section.

Vehicles need to be considered as a potential source of particle-bound transition metals in health-related studies. Table 6 provides illustrative data showing the metals content of diesel and gasoline emissions, and shows that IC engine emissions have significant metal content. Metals are reported in mg/mi for the average of two in-service diesel trucks sampled in 1996 in California[276] and for the average of four 1995 model-year Ford automobiles.[279] The variation in the data is large, and only the elements where Schauer et al.[276] reported a mean greater than twice the standard deviation are listed. The total mass emissions from the gasoline contain 9–31% metallic elements by weight. PM emissions of 27 elements from in-use high-emitting vehicles were reported by Cadle et al.[280]

Table 6. Metals emissions from internal combustion engines.

	Diesel Trucks	Automobiles
Total Mass	845 ± 22	7 ± 4
EC	260 ± 9	NR
OC	166 ± 6	NR
Si	5.3 ± 0.2	0.12 ± 0.12
Fe	0.42 ± 0.02	0.11 ± 0.09
Zn	0.59 ± 0.03	0.009 ± 0.005
S	1.86 ± 0.07	0.7 ± 0.9
SO_4^{2-}	8.5 ± 0.5	NR
NH_4^+	6.2 ± 0.3	NR

Notes: Emissions in mg/mi were calculated by the authors from data reported by Schauer et al.[276] and Ball.[279] NR = not reported.

Leaded gasoline has been phased out in the United States and in many developed countries, but it is still used. The particulate emissions from automobiles burning fuel with 0.4 g Pb/liter are about 25% Pb,[281] and the mass mean particle size is 1–2 μm,[248] which is much larger than the PM from spark ignition engines running on unleaded fuel. The Pb emissions are on the order of 60 mg/mi. The measured Pb concentration also reflects dilution by the higher EC and OC content of emissions from gasoline engines that are not equipped with modern pollution control technology. Use of methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane-boosting additive results in the emission of amorphous manganese sulfate and phosphate particles with a size ranging from 0.2 to 10 μm.[282]

Modern IC engines produce PM in both the ultrafine mode and in a larger accumulation mode, with nearly all the mass being in particles smaller than 1 μm. Emissions of PM, unburned hydrocarbons, NO_x, and CO all have declined as stricter regulations on new vehicle models have forced improvements in combustion technology and in post-combustion gas cleanup. The limits of current technology are being reached, and air-quality models are predicting an increase in total emissions from vehicles in the next decade as increases in vehicle-miles driven begin to outweigh the reductions in emissions that have been achieved by retiring older vehicles. Health concerns regarding particle number, ultrafines, and transition metals will lead to a need for more detailed characterization of IC engine emissions, especially under in-service conditions.

Aircraft Turbines

The aircraft PM emissions literature includes studies addressing both ground-level emissions near airports[283,284] and cruise altitude studies emphasizing stratospheric chemistry and global climate effects.[285–288] Visible smoke emissions from aircraft engines were first regulated by the 1970 Clean Air Act. The engine manufactures retrofitted jet aircraft with smokeless combustors by 1978,[289] and there is little published research on soot emissions from gas turbines from the late 1970s until the mid-1990s. Ground-level PM measurements show that most of the particle mass is soot and semivolatile products of incomplete combustion. Cruise altitude particle number is dominated by H_2SO_4 aerosol. Table 7 compares the mass, size, and number concentration for ground-level testing of engines representing 1970s[290] and 1990s[285] design technology. Conversion to smokeless combustion chamber designs has reduced particle mass and number concentration. However, aircraft engines still can be a locally significant source of submicron particles.

Table 7. Ground-level emissions from aircraft turbine engines.

	Stockham, 1979		Petzold, 1998[a]	
Engine Type	TF–30, JT8D, JT9D		Rolls Royce	
Particulate Mass	Idle	1.85–4.41g/kgfuel	Total carbon	
	Cruise	0.29–2.09	0.27–0.74 g/kg fuel	
	Takeoff	2.8–7.06		
Particle Size	Idle	0.043 μm	Primary	0.045 μm
	Cruise	0.69	Coagulation	0.18
	Takeoff	0.60	Coarse	0.56
Particle Number Concentration	Idle	$9.3 \times 10^7/cm^3$	Primary	$8 \times 10^5/cm^3$
	Cruise	2.27×10^7	Coagulation	$2.5 \times 10^4/cm^3$
	Takeoff	1.9×10^7	Coarse	$1.5 \times 10^3/cm^3$

[a]Particle number reported by Petzold was measured 200 m behind the engine and was not corrected for dilution.

EMISSIONS, AMBIENT CONCENTRATION, AND INHALATION EXPOSURE

The legal authority of air quality agencies extends only to the component of exposure that is attributable to ambient air,[291] and indoor air quality is controlled indirectly through public health advice, building codes, and product design regulations. Most of the average person's day is spent indoors or in vehicles, and sensitive individuals, infants, the sick, and the elderly spend even more time indoors than healthy working adults. Indoor particle concentrations can be very different from the outdoor ambient particle concentration that is measured by central monitoring stations. The indoor PM concentration and size distribution depend on the rate of outside air exchange, personal activity patterns, and indoor particle sources. In general, the concentration of coarse particles is lower indoors than outside, but activities such as sweeping, or even walking on a dusty carpet, can resuspend large quantities of coarse PM.

Institutional buildings have central air-handling systems that include filtration. A comparison of air samples in patient areas of three hospitals showed little correlation between indoor air PM_{10} and ambient PM_{10} at local air monitoring stations.[292] A better correlation is observed between indoor and outdoor fine-particle concentration. Accumulation mode ambient PM can penetrate into buildings because these particles are not efficiently removed by gravitational and inertial mechanisms. However, activities such as cooking and tobacco smoking are indoor PM sources that can increase fine-particle concentrations far above ambient levels. Personal exposure to particles depends on physical activity (ventilation rate) and on the amount of time spent in various environments indoors, in vehicles, and outdoors.

Health effects research must look at the actual human exposure, and many of the indoor sources involve combustion-generated particles. When discussing the health effects of combustion particles, one must consider that, with the exceptions of domestic combustion and tobacco smoking, people do not directly inhale combustion emissions. Persons inhale particles that have undergone post-combustion and atmospheric transformation. Different particle sizes are removed from the atmosphere at different rates, and the particles may become coated with condensable species. The cells deep in the lung are not exposed to the same particle mixture that is measured by an ambient filter, due to size-selective removal in the airway. Some gas-phase chemicals that would ordinarily be removed by diffusion to the airway wall may penetrate deep into the lung when adsorbed on an inert particle, the "Trojan Horse" hypothesis.

Ambient PM Characteristics

As originally reported by Whitby and Sverdrup,[293] and since confirmed by many studies, atmospheric particles have a multimodal size distribution, as shown in Figure 14.[6,293–296] These modes include the coarse mode, which is usually mechanically generated; the accumulation mode of 0.1–1 μm particles; and a mode of fine particles resulting from nucleation and surface growth. The latter two modes are the consequence of nucleation, condensation, and coagulation to produce particles from gas-phase precursors. The true accumulation mode is the result of particles growing into the range where further growth is slow, because of decreased collision frequency, and where removal is slow, because inertial deposition and gravity settling are inefficient. The size and shape of the ultrafine particle mode in the urban atmosphere represents a dynamic balance between the generation of new particles (nuclei) by nearby sources and growth into the accumulation mode by coagulation and surface deposition.

The process of forming new particles by nucleation and the subsequent growth by coagulation and condensation are similar both in combustion systems and in the atmosphere. Nanoparticles are created from vaporized compounds by gas-to-particle conversion due to chemical reaction or cooling. These reactions may take place in the combustor, during initial dilution of the plume, or over a period of hours in the atmosphere. Nanoparticles are rapidly removed from the atmosphere by coagulation

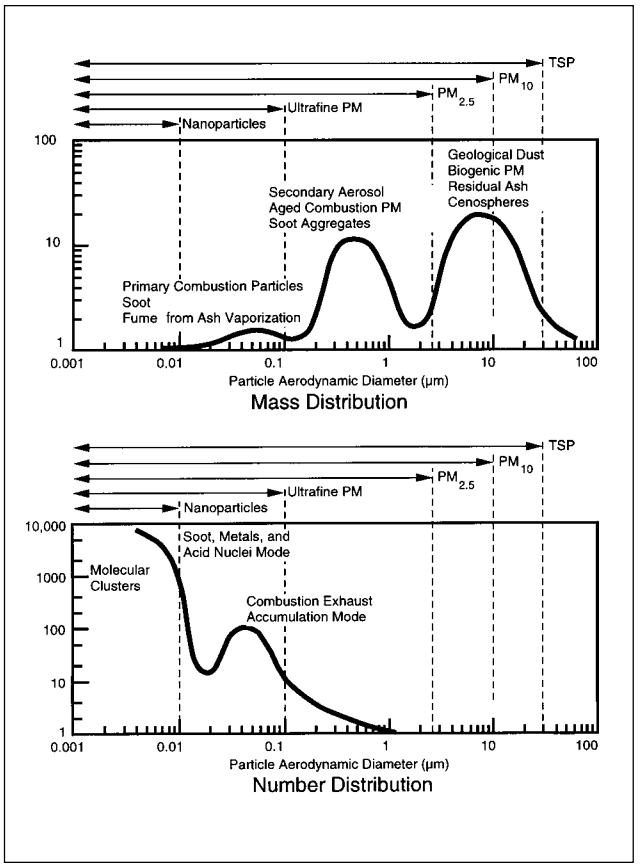

Figure 14. Typical PM mass and number distributions showing the multimodal nature of the ambient aerosol. Adapted from data by refs 6 and 293–295.

with each other and with larger particles. In addition, species condensing from the gas phase are deposited on ultrafine particles since they represent a large fraction of the available surface area. These condensing species include organic compounds, SO_4^{2-}, and NO_3^- formed by reactions in the atmosphere from precursors that are emitted as gases from combustion systems. Eventually, the ultrafine nuclei-mode mass is transferred into the accumulation mode consisting of particles between 0.1- and 1-μm diameter. Accurately measuring the ultrafine size distribution, in both the ambient air and combustion source emissions, is difficult because particle number is not conserved, ultrafine particles undergo rapid transformations, and there are few calibration standards available. Seinfeld and Pandis provide a detailed treatment of ambient aerosol characteristics.[6]

Gravimetric measurements of particle mass generally show only the coarse and accumulation modes unless the data are plotted on a logarithmic scale. Likewise, optical and electrical mobility measurements of particle number usually show only the nucleation and accumulation modes. Natural PM includes wind-transported geological material, biogenic PM (pollen, spores, and secondary PM from VOCs), and sea salt. Naturally released sulfur and nitrogen compounds produce additional PM, but the anthropogenic emissions of sulfur and nitrogen compounds dominate secondary particle formation in industrialized areas. Comparison of oceanic, polar, and remote desert aerosols[297] to urban aerosols[293] shows that the natural nucleation and accumulation modes are small compared to the anthropogenic contribution to fine PM. Reported concentrations of ultrafines in ambient air vary from 100 to 1000/cm^3 in rural and oceanic environments, 10^4/cm^3 time-averaged in urban areas,[298] and ~10^6/cm^3 near an urban freeway.[6] Janecke[297] provides quantitative descriptions of typical ambient aerosols as the sum of three lognormal distributions, which are useful for modeling input.

Source Apportionment and Modeling

Figure 15 shows that 80–90% of the PM mass emitted from combustion sources is below 1-μm diameter, while less than 10% of the mass of dust from geological material is $PM_{2.5}$.[294] However, the evidence for the relative contribution of various $PM_{2.5}$ sources is contradictory, and some source apportionment studies[299] suggest that ambient $PM_{2.5}$ is dominated by sources other than combustion particles. For example, Figure 16 shows ~62% of emissions coming from geological material and only 38% coming from combustion sources.[300,301] Emissions inventories are based on multiplying census-type data by emission

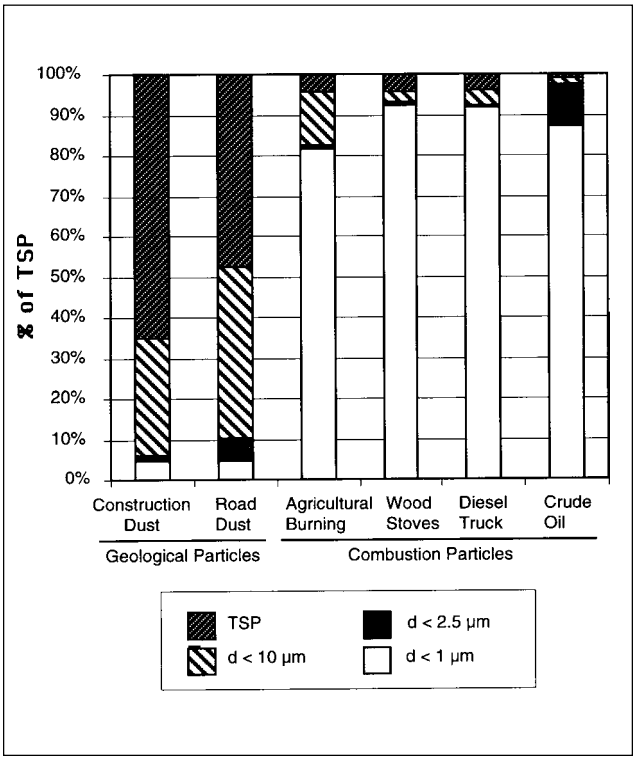

Figure 15. Typical size distribution for the emissions from geological dust sources and from combustion sources. PM_1 dominates the mass of combustion emissions, while most geological dust is larger than PM_{10}. Replotted from data in Watson and Chow.[294]

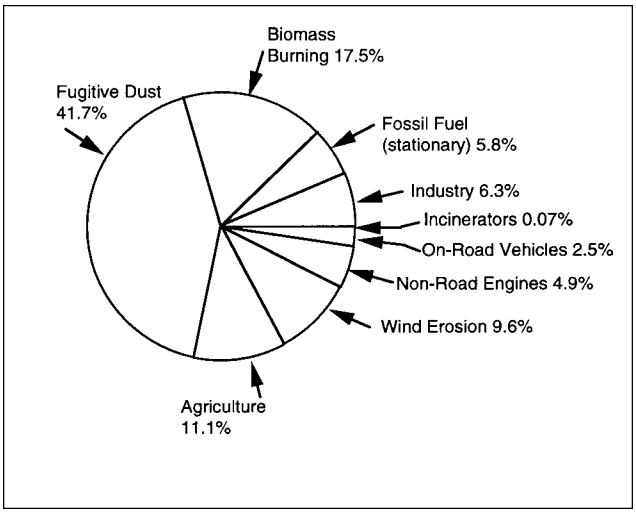

Figure 16. Inventory of the 1997 U.S. nationwide $PM_{2.5}$ emissions.[300] Total mass was estimated as 10 Tg/yr. Major differences exist between inventory data and source apportionments based on the composition of particles collected at receptor sites. Source: U.S. Environmental Protection Agency.

factors, which are often based on only a few measurements. Both researchers and air quality agencies suspect that the fugitive dust component is overstated by these methods.[294] If the fugitive dust is overstated, then some other contribution, such as combustion, is understated, as many urban areas are in violation of the PM standards. Suspected sources of the differences between emissions inventory and receptor-based methods of calculating source contributions include comparing national averages which are dominated by rural areas with monitoring stations which are concentrated in urban areas; not fully accounting for redeposition of windblown PM near the source area; and not including the effect of "super-emitter" sources such as improperly maintained and operated combustion sources in the inventory emission factors.

As EPA compiles information from speciated PM monitoring sites, it will be interesting to learn more about the chemical characteristics of ambient PM and how this can relate to specific sources, including combustion. International variation in the relative contribution of combustion and geological processes to ambient PM are expected because of local climate, geography, and technology preferences. For example, in urban areas in Taiwan, $PM_{2.5}$ was found to be as high as 80–90% of PM_{10},[302] and combustion was found to be a major source of both the coarse and fine PM.[303] Likewise, particles larger than 2.5 μm, or even larger than 0.5 μm, are rare in the central European urban environment.[304]

The combination of particle size and chemical composition data provides insights into the sources. For example, the $PM_{2.5}$ in the eastern United States has a much larger SO_4^{2-} component and a much smaller NO_3^- component than does the $PM_{2.5}$ from California.[305] This result is likely due to the effects of coal-fired power plants in the east and of agriculture and mobile sources in the west. Source apportionment based on matching chemical composition of particles collected from known sources with the mixture collected at receptor sites is an active area of research.[294,306–308] Reconciling source inventories with the particles actually collected at receptor sites has important public policy implications.

A mechanistic air quality model has been developed that allows computing the contribution of individual emission source types to the size and chemical-composition aerosol distributions.[309] The model predicts that the submicron fraction of the PM does not contain appreciable amounts of secondary particles. Specifically, little SO_4^{2-} and no NO_3^- was predicted in the particles less than 0.1 μm. For particles between 0.1 and 1 μm, SO_4^{2-} concentration was slightly higher with a larger increase in NO_3^- concentration. Data from filters confirmed the modeling results,[310] although the sulfur concentration in the particles less than 0.1 μm was higher on the filters than predicted. The model explains the measured 0.2- to 0.3-μm particles as transformed emissions from diesel engines and other combustion, and explains the observed 0.7- to 0.8-μm particles as fine background aerosol that has been transformed by fog and gas-to-particle conversion in the urban air.[310] The model predictions are only as accurate as the source data and the atmospheric transformation chemistry models.

The observed particle size distribution in urban environments is the result of a dynamic balance between generation of ultrafine particles by combustion sources and the transfer of these particles to the accumulation mode by coagulation and by surface growth from secondary aerosol gas to particle conversion. While computational modeling may provide insights into the relationships between sources and human exposure, models are limited by the source data, and there is a need for more detailed characterization of combustion sources.

PARTICLE HEALTH EFFECT RESEARCH

Particles have long been implicated in the deterioration of visibility and the environment and as the cause of adverse health effects. As early as 1661, John Evelyn wrote,[311] "It is this horrid smoake, which obscures our churches and makes our palaces look old, which fouls our clothes and corrupts the waters so that the very rain and refreshing dews which fall in the several seasons precipitate this impure vapour, which with its black and tenacious quality, spots and contaminates whatever is exposed to it." Evelyn goes on to say, "London fires, there results a great quantity of volatile Salts, which being sharp and dissipated

by the Smoake doth infect the Aer, and so incorporate with it, that though the very Bodies of those corrosive particles escape our perception, yet we soon find their effects, by the destruction of all things they do but touch; with their fuliginous qualities." Evelyn not only implicated combustion, but also inferred that the cause was from small particles.

This section discusses the ongoing research into the health effects of particulate air pollution, with an emphasis on the toxicological hypotheses that relate to specific types of combustion-generated particles. Table 8 summarizes combustion particle characteristics that are suspected to be important for health effects and the results of selected epidemiology and toxicology studies that have addressed these physical and chemical characteristics.[6,8,25,213,305,308,312–348] Recent reviews discuss the toxicologic and epidemiologic evidence for health risks from gasoline and diesel engine emissions;[324,349] the toxicology of ultrafine anthropogenic atmospheric aerosols;[345] and the relationship of particle air pollution to asthma.[350] The proceedings of recent conferences are sources of more detailed coverage of current health-related research.[351,352]

Table 8. Combustion particle characteristics investigated in toxicology studies.

Characteristic	Relation to Combustion	Epidemiology Studies	Toxicology Studies
Mass	Filterable combustion aerosols are a minor component of urban aerosol, which is dominated by organic, secondary, and geological PM.[305]	Health outcomes have been associated with ambient PM mass.[340]	Exposure of young, healthy adults to concentrated ambient particle does not cause acute effects.[323,336]
Particle Size	Combustion is the major source of submicron and ultrafine PM. (This review.)	Coarse particles are not associated with mortality,[338,341] but health outcomes are associated with fine PM.[318]	Iron mobilization from coal fly ash in cell culture increases with decreasing particle size.[343] Mutagenic activity is associated with fine PM.[333]
Ultrafine and Nanoparticles	Inorganic ultrafines are formed by mineral vaporization during combustion followed by nucleation and condensation. (This review.)	Respiratory effects associated with ultrafine PM number.[335,345]	Differences between fine and ultrafine particles of the same material.[319,331,332,346]
Transition Metals	Submicron particles from combustion are enriched in transition metals. Fe is more bioavailable from coal fly ash than from geological dust with similar size and total Fe.[348]	Associations of health outcomes and transition metals were found in some studies,[327,334] but not in others.[325]	Transition metals catalyze formation of reactive oxygen species.[326,342] Metals from ambient PM[314,322] and coal fly ash[344] induce synthesis of proinflammatory cytokines in cells and lung inflammation in rats.[317]
EC (Soot)	Combustion produces 10- to 50-nm diameter carbon-rich primary particles. (This review.) Diesel exhaust is the major source of urban soot.[308]	Weak association between diesel exhaust and cancer risk[324] but uncertain dose-response relationship.[347]	Carbon black and whole diesel exhaust produced similar lung lesions in rats.[330] Ultrafine carbon causes lung inflammation.[329]
OC	Incomplete combustion produces a wide range of organic species.[213,312]	Exposure studies[324] to whole diesel exhaust include the soluble organic fraction.	PAH compounds include known and suspected carcinogens and mutagens.[324,328]
Secondary SO_4^{2-} and NO_3^-	Most of the urban ambient $PM_{2.5}$ is secondary aerosol formed from combustion-generated SO_2 and NO_x.[6,8]	SO_4^{2-} and NO_3^- are implicated by studies that correlated risk with PM mass.[318]	NO_3^- not toxic at 1 mg/m^3 agricultural worker exposure.[313] High levels of SO_4^{2-} associated with increased airway resistance.[315]
Acidity	Cl and S in fuels produce HCl and SO_2 in the combustion products.	Some evidence for a correlation of health outcomes with H^+.[340]	Various responses reported to laboratory inhalation of acid aerosols.[321]
Synergistic Effects	Combustion emissions contain EC, OC, metal-rich particles, CO, and acid gases.	Epidemiologic studies are confounded by the complex mixture of pollutants in ambient air.[337,339]	Exposure to pairs of pollutants can produce greater effect than either one alone: ultrafine PM and O_3,[320] coal fly ash and H_2SO_4,[25] benzo[a]pyrene and carbon black.[316]

Epidemiology

Epidemiology, the medical science that investigates the quantitative factors controlling the frequency and distribution of disease, provided the initial evidence that the PM_{10} ambient air standard did not meet the legal criteria in the Clean Air Act to "protect the public health" while "allowing an adequate margin of safety."[353] The current emphasis on the health effects of particulate air pollution was set in motion by the seminal studies of Pope, Schwartz, and Dockery. Pope compared hospital records for years when a steel mill in Utah was operating and closed and showed that elevated PM_{10} concentration was associated with increased hospital admissions for pneumonia, pleurisy, bronchitis, and asthma.[354] Schwartz and Dockery showed that variation in total suspended PM correlated with the number of deaths per day in Steubenville, OH, over an 11-year period.[340] Dockery et al. showed that fine-particulate air pollution, or a factor correlated with fine PM, contributed to excess mortality in six U.S. cities.[318]

The methods used in recent air pollution epidemiology studies have been reviewed,[355,356] and these methods are based on general correlation models described in advanced statistics texts.[357] Several studies have involved reexamining previous results by an independent group of investigators to verify the conclusions by alternative statistical methods.[358,359] The statistical association of fine PM and various health end points appears to be robust, that is, independent of the specific correlation model used. Pope reviewed epidemiology studies of particulate air pollution from 1953–1996 and listed approximate ranges of estimated effects.[337,355] For a 10-$\mu g/m^3$ increase in PM_{10}, the effects were a 1.5–4.0% increase in respiratory mortality, a 0.5–2.0% increase in cardiovascular mortality, a 0.5–4.0% increase in respiratory hospital admissions, and a 1.0–4.0% increase in grade-school absences. Detecting such a small increase requires an extremely sensitive statistical method. Since the average death rate in the United States is about 20 deaths/day/million persons, a 1% increase in mortality represents 1–2 excess deaths above the daily average in a metropolitan area containing 5 million people.

Epidemiology methods have limitations. These studies can only correlate data that have been consistently measured over a sufficient geographical area or period of time to show detectable variation. For example, to test for the effect of geological particles, studies have had to use indirect measures of wind-blown dust such as the dates of dust storms[341] or the atmospheric clearing index.[338] Epidemiologists have not correlated health effects with either ultrafine ambient particles or with the ambient concentration of biologically available transition metals because these suspect particle characteristics have not been routinely measured. Although epidemiology can show a correlation, it cannot prove causality. Two well-correlated factors may both be individually correlated with a third unknown factor that is the actual cause. There have been frequent suggestions that the observed health effects that have been correlated with particles are actually due to another pollutant that correlates with PM. Stagnant air conditions in urban areas can lead to the simultaneous buildup of multiple pollutants including PM, O_3, SO_2, CO, soot, and numerous gas-phase and particle-bound organic species, so this is a reasonable hypothesis. As will be discussed in the measurements section of this review, a need exists for the development of robust, precise, economical methods for measuring the various particle characteristics that are possible factors for health studies.

Epidemiology studies in Spokane, WA,[341] and in Utah[338] suggest that coarse, wind-blown particles are not the cause of the observed health effects. This implies that some other component of the urban PM, such as fine particles from combustion, is related to the observed effects. An important distinction must be made between chronic and acute health effects. Some health effects, such as chronic bronchitis, emphysema, pneumoconiosis, fibrosis, and lung cancer, are associated with many years of exposure to the combustion emissions or other inhalable toxic agents. The acute effects of particle inhalation include hospital admissions associated with asthma, bronchitis, pleurisy, pneumonia, and cardiovascular disease. Time-series epidemiology studies show that these effects typically lag the changes in PM level by 1–5 days.[355] During the 1952 London Fog event, a temperature inversion trapped the air pollution, allowing the buildup of combustion emissions to lethal concentrations over a period of four days in December. The increase in deaths was almost 4-fold during the episode, and the effects started within a day of the onset of the pollution increase.

The mass concentration increments addressed by ambient air epidemiology studies are orders of magnitude below the inhalable particle concentrations for PM in occupational settings. Average concentrations of diesel PM ranging up to 1400 $\mu g/m^3$ have been reported in studies of underground mines.[360] Typical allowable 8-hr concentrations for general "nuisance dusts" in occupational settings range from 2000 to 10,000 $\mu g/m^3$, and these measurements are usually stated in mg.[361] Few papers have proposed toxicological mechanisms that are based on particle mass alone at ambient concentrations. Particle mass, which has been the focus of most ambient PM epidemiology, is likely to be a surrogate for the real agent. However, Harrison and Yin,[362] in a review of PM health effects, discussed the uniformity of epidemiologic correlations between PM concentration and health end points observed in different regions of the world with different proportions of SO_4^{2-}, NO_3^-, crustal material, and other

major PM components. They concluded that the available data provides little support for the idea that any single major or trace component of PM is responsible for adverse effects, but acknowledged that there is evidence that particle size rather than mass may be the appropriate measure to correlate with health effects.

Respiration and Particle Inhalation

The respiratory system will be briefly discussed to provide a background for the discussion of human population, whole animal, and cell culture studies of combustion particles. Concise descriptions of the human respiratory system, written in the context of air pollution engineering, include those by Carel[363] and Degobert.[248] Guyton and Hall's textbook is recommended for a comprehensive introduction to cardiopulmonary physiology,[364] while Netter's collection of illustrations is recommended for visualizing respiratory anatomy.[365]

The observed statistical associations of ambient PM mass concentration with morbidity and mortality lead to the mechanistic question: How can a small increase in the mass of inhaled particles deposited cause sickness or premature death? A person inhales from 6 to over 12 m^3/day of ambient air, depending on age and physical activity. This air contains a wide variety of natural particles from geological and biological sources as well as anthropogenic pollutants. The deposition of supermicron particles by inertial impaction and of submicron particles by diffusion depends on the gas velocity and residence time in various sections of the airway and lung. A widely used model of size-dependent deposition in the nasopharyngeal, tracheo-bronchial, and pulmonary regions of the respiratory system[366] is reproduced in many references, for example, Wilson and Spengler.[367] Most of the PM_{10} mass is deposited in the nose and throat, while ~60% of inhaled $PM_{0.1}$ is deposited in the lung. Actual size-dependent particle deposition depends on age, health, and especially on nasal versus oral breathing.[368]

Assuming typical values for respiratory volume and alveolar deposition efficiency, a calculation shows that a 10-$\mu g/m^3$ increment in ambient $PM_{2.5}$ results in an increment of 0.02–0.05 mg of particles deposited in the lung per day. This has lead to the opinion that either some component of ambient PM is highly toxic or that some individuals are highly susceptible. Alternatively, particle number may be considered. Assuming typical values for ventilation rate, lung surface area, and epithelial cell size, a calculation indicates that a typical urban, near-highway concentration of 10^5 particles/cm^3 results in an alveolar deposition rate of ~1 particle per cell per day. Figure 17 shows the relative size of the microscale structures in the alveolar region of the lung compared to a range of ambient particles.[364,365,369] The accompanying graphs in Figure 17 show a typical urban aerosol mass distribution and the calculated number of particles deposited per alveolus per day as a function of size. The calculated deposition assumes an ambient concentration of 100 $\mu g/m^3$ of PM_{10}, with 40% of the mass being smaller than 2.5 μm, and 2% being smaller than 0.1 μm. The deposition is calculated using the size-dependent deposition fraction[366] and assumes uniform deposition to all alveoli. This analysis shows that fewer than 1 in 1000 alveoli has a coarse particle deposited per day, but that a typical alveolus may be exposed to several hundred ultrafine particles per day.

The body has defenses to rapidly remove inhaled particles. A mucus layer, moved upward by cilia on the cells lining the airways, transports particles from the respiratory system to the throat, where they can be coughed up or swallowed. The terminal airways and alveoli lack ciliated cells. Mobile macrophage cells take up particles by phagocytosis and remove the particles from the alveoli by active transport into the ciliated airways. Particles are also removed from the lung by dissolution and by transport into the lymphatic drainage system. A fraction of the inhaled particles is retained for a long time in the respiratory system, either in the airways or in the interstitial spaces. The process of clearing particles from the lungs can induce secondary physiological responses including coughing and inflammation. The mammalian respiratory system is likely to have evolved clearance mechanisms that are appropriate for the natural background particle number concentrations. A plausible hypothesis is that the large numbers of ultrafine particles in the urban aerosol may simply overload the ability to clear particles from the lungs. Alternatively, some specific types of inhaled particles may interact with the body's nervous and biochemical signaling pathways, resulting in an amplified response.

Identification of specific particle types in the ambient mixture that are biologically active for specific health effects is an active area of research.[2,3] The effects of inhaled particles may increase with decreasing particle size due to several factors: finer particles are deposited in the lung rather than in the upper airway; finer particles have greater surface area per unit mass, which enhances solubility; and finer particles can enter cells more readily and can be transported from the lung to other organs. The living cell interacts with the surface of a particle, so surface chemistry, not the volume average composition, is likely to be most relevant for biological effects of low-solubility particles.

Controlled Exposure to Concentrated Ambient Particles

Inhalation exposure studies complement the results of epidemiology studies. The effect of particulate air pollution

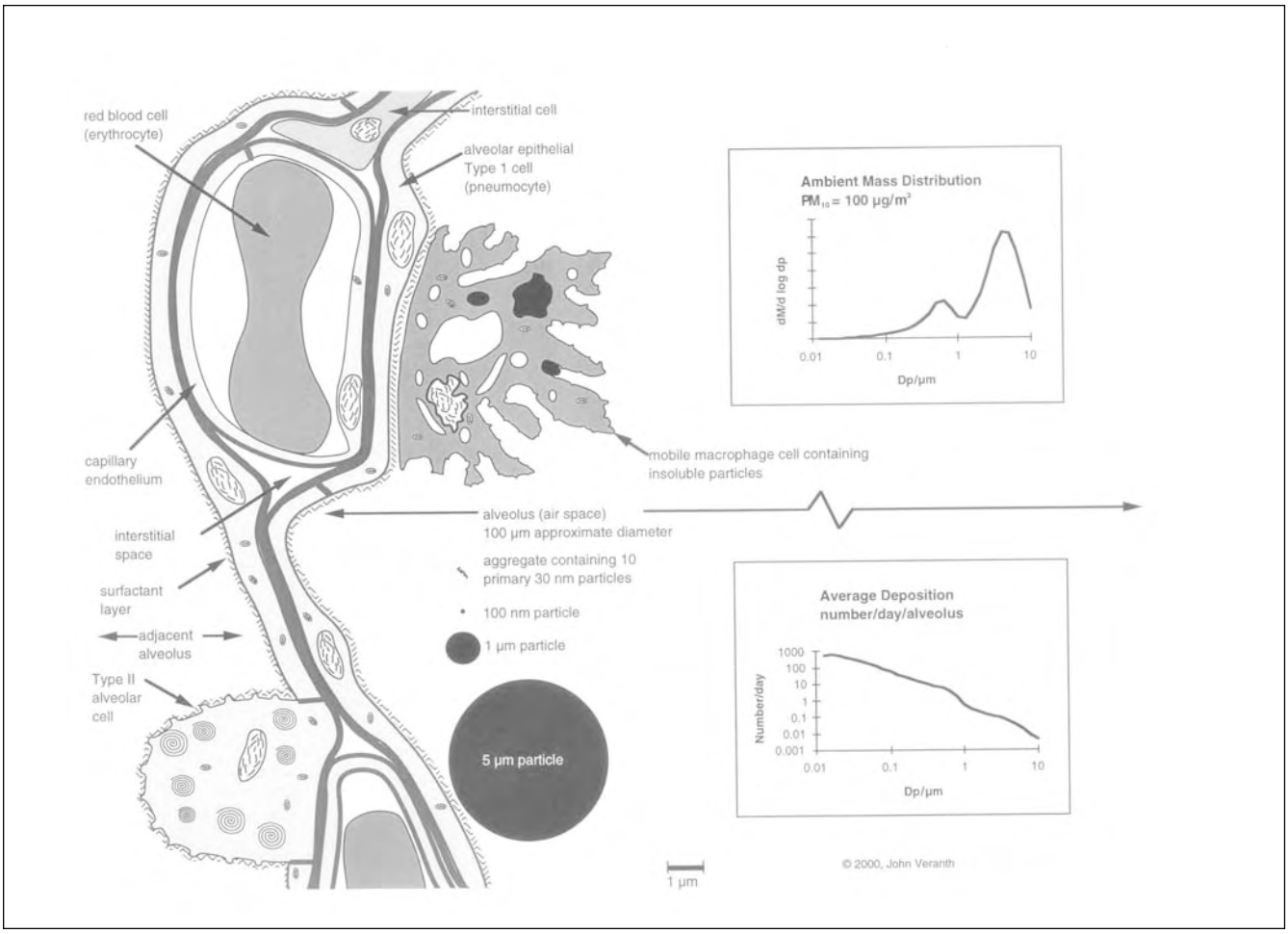

Figure 17. Scale drawing comparing ambient particles to structures in the aveoli of the human lung. The graphs show a typical ambient PM mass distribution and the expected number of particles of each size deposited per alveolus per day. Submicron particles are suspected to be important for health effects because of the large number deposited in the lung and because these particles can move into the interstitial space and blood stream. Compiled from information in refs 364, 365, 369.

can be amplified by conducting controlled inhalation exposure studies with concentrated ambient PM. This has been facilitated by the development of virtual impactor particle concentrators[370–372] and centrifugal particle concentrators[373] that keep the aerosol suspended while separating the gas from the particles. These particle concentrators can be staged to supply an inhalation chamber with air containing a 10-fold or higher concentration of ambient PM. Studies of this type are being conducted with both human volunteers[323] and with laboratory animals.[374,375] An early conclusion is that healthy adults show no adverse impacts from short duration exposure to concentrated ambient particles.[323,326]

Laboratory Studies with Surrogate Particles

A disadvantage of both epidemiologic studies and studies using concentrated ambient PM is that the subject is exposed to a complex mixture containing contributions from many sources, most of which are unknown or poorly characterized. An alternative is to conduct studies with laboratory-generated surrogate particles from well-characterized sources. This approach is most appropriate for conducting mechanistic hypothesis-based toxicological experiments, since the investigator can specify the particle characteristics used for the test and control condition pairs. An example of this type of study involved supplying fresh laboratory-generated coal fly ash particles to animal inhalation chambers as part of a study of the combined effects of H_2SO_4 and coal fly ash.[25,376] Inhalation studies involving ultrafine and nanoparticle PM also require having a laboratory particle generator connected to the inhalation chamber due to the rapid transformation of the particles by coagulation.[377] Surrogate particle inhalation studies require close cooperation between the life sciences and aerosol team members as well as physical proximity of the animal care and combustion facilities. Due to the cost and complexity of conducting animal inhalation studies at combustion facilities, alternative experimental methods are common.

Inhalation of resuspended particles allows the particle generation and collection to be separated from the exposure studies. There is little difficulty in resuspending 2.5- to 10-μm aerosol particles, and resuspension is also suitable for testing hypotheses related to particle chemical composition if particles with size-independent composition are available. Surface forces make the dispersion of submicron particles difficult, so resuspension has serious disadvantages if the hypothesis involves testing size-dependent effects. Improved methods for particle resuspension have been developed.[378–380]

Alternatively, particles may be instilled into the lung as a suspension in saline solution. Despite the artifacts introduced by this invasive procedure, instillation studies have been used to investigate combustion particle effects.[317,329,331,381] Cell culture studies involve mammalian cells or bacteria growing in an appropriate medium. Normally, the cells grow as a layer on the bottom of the culture dish or flask. The cells can be systematically exposed to various types of combustion particles or particle extracts to test specific biochemical hypotheses.[314,382] The biochemistry of single cells, especially cell lines derived from tumors, can differ from the responses that occur in the normal whole animal. Also, cell culture studies do not include any effects related to the interaction of the respiratory tract and nervous system with the particles.

In vitro experiments performed with purified chemicals under cell-free conditions can isolate specific mechanism steps such as the rate of mass transfer of a potentially toxic component from a combustion particle. But even experiments that simulate physiologically relevant conditions simulate only a fraction of the biochemistry that takes place in a living organism.

Laboratory experiments with surrogate particles can be conducted in vitro, using cell-free models of selected biochemical steps; in cell culture, using established cell lines; and in animal models of the human respiratory system. Specific mechanistic hypotheses can be tested by using well-characterized particles from known sources. These types of studies provide an important link between fundamental biochemistry and human population studies. The next section will discuss some of the hypotheses that are topics of current PM research.

Cardiopulmonary Effects of Particles

An active hypothesis is that the observed cardiac symptoms associated with particle inhalation may be mediated by the nervous system. Certain nervous system-activated changes in heart rate, blood pressure, blood viscosity, and heart-rate variability are associated with an increased likelihood of sudden cardiac death.[383] A study of 90 elderly subjects showed that changes in blood oxygen saturation were not associated with exposure to particle air pollution, but increased pulse rate was associated with exposure to particle air pollution on the previous 1–5 days.[384] A decline in heart-rate variability is a quantitative indication of impairment of the autonomic function, that is, a decline in the ability of the cardiorespiratory system to respond to changes. A decrease in heart-rate variability has been observed for persons exposed to increased ambient PM_{10} in Utah[385] and to increased $PM_{2.5}$ in the Boston area.[386] Cardiac monitoring may provide a sensitive indication of acute response that will be useful in identifying the relative importance of different components of ambient aerosol. Exposure of dogs with induced coronary occlusion to concentrated ambient particles affected one of the major electrocardiogram signs of myocardial ischemia,[375] and other cardiac and respiratory parameters were also affected. This suggests a plausible mechanism by which persons with existing heart disease may become more susceptible to serious cardiac effects when they are exposed to some component of ambient PM.

Biochemical Signaling

The nervous system and other biological signaling pathways can result in enormous amplification of a stimulus. Persons with hay fever or asthma are familiar with the massive response that can occur within minutes of exposure to an allergen. Cytokines are intracellular signaling molecules that mediate many protective physiological functions such as increasing the blood circulation and recruiting leukocytes (white blood cells) at the site of an infection. Cytokines can also induce potentially harmful responses such as prolonged tissue inflammation and development of fibrosis in response to irritants.[387,388] Lung inflammation has been associated with exposure to elevated ambient PM,[389,390] and a number of studies are focusing on the relationship of inhalable particles to the biochemical events leading to lung inflammation.[158,317,326,344,391–394] Combustion particles may contain specific chemical species that are able to activate biological signaling pathways, and a number of these hypotheses involve transition metals.

Transition Metals and Biochemical Processes

Particles provide a vehicle for metals to enter the body in inappropriate amounts. Much of the literature on the toxicity of solid-phase metal compounds is based on ingestion rather than on inhalation.[395] Ingestion dose-response relationships may be relevant for the effects of larger particles that are deposited in the upper airways but are rapidly cleared from the respiratory system to the throat, where they are swallowed. However, submicron particles are deposited deep in the lung, and ultrafine particles are able to pass from the lung directly into the body.[331] There is increasing evidence that the same element has very

different behavior when inhaled than when ingested. Mn, a necessary trace mineral in the diet and a controversial octane-boosting additive in gasoline,[396] provides an example. Dietary Mn is homeostatically regulated by the liver, and ~3% of ingested Mn is absorbed.[397] Inhalation bypasses the digestive system, and up to 40% of inhaled Mn is absorbed.[398]

The dose of a particle-bound element that is available to the body depends on the entry route, the particle size and morphology, and the mineral species in the particle. When conducting laboratory experiments on metal bioavailability, it is necessary to distinguish between in vitro, extracellular, and intracellular behavior, since the solubility of transition metals from a given combustion ash mineral species depends on the pH and the presence of chelators. Many chelators are present in cells, and some, such as citrate, are present at millimolar concentrations.

Transition metals on inhaled particles may act as biochemical catalysts that can induce other biochemical responses. Transition metals, such as V, Cu, Fe, and Pt, can catalyze the generation of ROS[399] that have been associated with both direct molecular damage and with the induction of biochemical synthesis pathways. Coal fly ash and residual oil fly ash have been studied as examples of combustion particles enriched in transition metals. Residual oil fly ash has been shown to induce inflammatory cytokines in human bronchial epithelial cells[314] and both lung inflammation[326] and cardiac arrhythmia[158] in inhalation studies with rats. Coal fly ash has been shown to be a source of bioavailable iron[343] and can also induce inflammatory cytokines in human lung epithelial cells.[344] Generation of ROS and induction of cytokines in human bronchial cells has also been reported in studies of diesel exhaust particles.[400] The amount of bioavailable transition metals contained in particles has been associated with acute lung inflammation from both combustion and ambient particles.[317] Studies have considered the water-soluble transition metals,[159] metals associated with organic material,[392] and metals that can be mobilized by an intracellular chelator at physiological conditions.[342]

A study of ROS generation in polymorphonuclear leukocytes (a white blood cell type frequently found in the airways of persons exposed to particles) using oil fly ash, coal fly ash, carbon black, natural dust, and ambient particles reported that the ROS correlated with the fraction of Si, Fe, Mn, Ti, and Co that was not removed by distilled-water washing.[401] In studies with coal fly ash and geological dusts,[402] the amount of bioavailable Fe under physiologically relevant in vitro conditions did not correlate with the total Fe in the particles, as shown in Figure 18.[342,343,403,404] Cultured human lung epithelial cells (Type A549) were exposed to PM_1-enriched coal fly ash

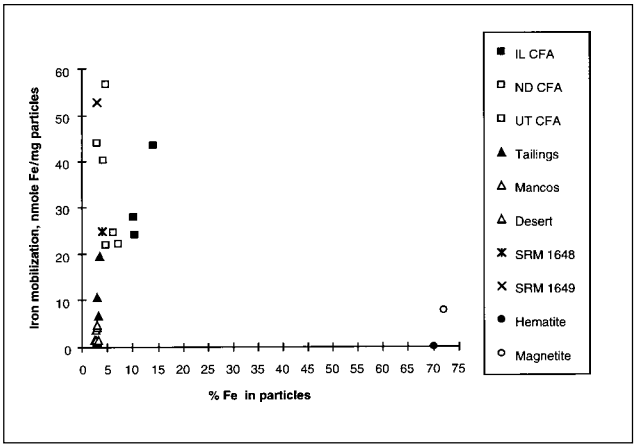

Figure 18. Iron mobilized by the chelator citrate and physiological pH from three types of coal fly ash, two types of dust from unpaved desert roads, mine tailings, urban particles, and pure iron oxides. The mobilized iron does not correlate with the total iron in the particles. Data sources: urban particles,[342] CFA,[343] geological dusts,[403] iron oxides.[404]

both as-collected and after pretreatment with the chelator desferrioxamine B. The chelator removed the ability of the coal fly ash to induce the synthesis of the proinflammatory cytokine IL-8.[344] Mössbauer spectroscopy of the coal fly ash before and after the desferrioxamine B treatment showed that Fe in an aluminosilicate glass phase was preferentially removed.[348] Fe in aluminosilicate glass occurs in combustion ash that is produced by rapid quenching from high temperature, but is not commonly found in dusts with similar elemental composition that have been produced by geological weathering.

Traditional mass transfer and heterogeneous chemical reaction theory[405] was applied to analysis of the measured rate of Fe mobilization from various sizes of coal fly ash by the chelator citrate. The rate of Fe mobilization was consistent with solid-phase-limited diffusion mass transfer, but the final values were consistent with size-dependent differences in initial composition.[402] Such size-dependent composition differences are expected from the mechanism of coal fly ash formation described in the fundamentals section above. These results show the importance of particle size and chemical speciation in the activation of specific biochemical pathways and suggest mechanistic reasons for differences in the response of the body to combustion and geological particles.

Soot and Biochemical Processes

Soot is the major type of combustion-derived ultrafine PM, and associated organic and inorganic compounds cause soot to have mutagenic, carcinogenic, and irritant properties. A study of size-fractionated urban PM showed that the mutagenic activity increased with decreasing particle size,[333] which is consistent with expectations for organic compounds

condensed on submicron combustion particles. The indeterminate chemical composition of the EC and OC mixture emitted from combustion, ranging from fuel-like hydrocarbons to primary particles formed from graphite-like fused aromatic rings, greatly complicates biochemical studies. Carbon black is often used as a surrogate for the EC component of real combustion soot.[329,330] Various solvent extracts of soot, or isolated compounds such as specific PAH species, have been used as surrogates in toxicological studies of the OC fraction of combustion soot. Many PAHs are suspected carcinogens and mutagens,[406] and there has been considerable controversy regarding the role of nitroaromatic compounds because of the differing results in bacteria and mammalian cells.[407] Quantified compounds account for only a fraction of the observed mutagenicity of real soot mixtures.

Chlorinated polycyclic aromatic compounds, especially polychlorinated dibenzo-p-dioxins, and furans are also associated with combustion emissions. These compounds are fat-soluble, accumulate up the food chain, and have been suspected to disrupt or mimic the action of developmental hormones.[408] The most-studied effects involve chronic exposure, but the possibility of acute effects from these compounds cannot be ruled out. The chlorinated dioxin and furan compounds are a special concern for municipal and medical waste incineration.[231] Emissions of chlorinated dioxin and furan compounds do not appear to be a problem when burning fuels that contain more sulfur than chlorine, such as coal.

Ultrafines

Ultrafine particles and nanoparticles have been proposed by some health researchers[377] as the biologically important ambient particle. Ultrafine particles are deposited by diffusion deep in the lung and have been found by Oberdörster et al.[331] to be retained in the lungs. Ultrafine particles can also pass through the cells lining the lung and enter the interstitial space. Table 9 summarizes studies with micron-sized and ultrafine particles of the same compound.[319,329,331,409–411] The data show that ultrafine particles often have a greater biological effect than an equal mass of larger particles of the same substance.

For slightly soluble particles, the high surface area of ultrafine and nanoparticles can result in a faster release of toxic compound than would result from larger particles of the same composition. The concentration of a toxic substance reached in cells or in body fluids is the dynamic result of the relative rates of release from the particle and of clearance of the toxic material from the body.

Synergistic Effects

The combination of multiple toxic substances often has a much greater effect than the sum of the effects of the individual substances. Historically, emissions of combustion particle and sulfur oxides have been closely linked. Separating the effects of these pollutants was difficult since both were produced from burning coal. Coal was used extensively in urban areas for both industrial steam engines and domestic heating in Europe and North America prior to the 1950s, when natural-gas pipelines, automobiles, and regulations for large industrial sources changed the emission pattern. European regulations treated these pollutants as a combination and set a limit on SO_2 that varied with the smoke concentration (roughly a measure of EC).[362,412] The assumption underlying this approach was that acid gases adsorbed on the surface of particles could be transported into the lung, whereas vapor-phase acid would diffuse to the wall of the upper respiratory tract. Amdur and coworkers conducted extensive studies of the health effects of H_2SO_4 aerosols, both as a pure component and in combination with coal fly ash.[25,26,413]

Amdur[25,26] reported that a 10-fold increase in dose with acid aerosol alone was required to match the effect on lung-diffusing capacity caused by inhalation of H_2SO_4 condensed on PM. A concentration of 310 mg/m^3 of H_2SO_4 mist corresponded to the same change in diffusion capacity as occurred when the H_2SO_4 was surface-layered on a coal fly ash particle at a concentration of 30 mg/m^3. In addition, the type of particle was also important. Amdur found that with lignite, which has higher Ca and Na than does bituminous coal, the H_2SO_4 reacted with the alkali to form sulfates. With bituminous coal, which has Al, Si, and Fe-rich ash, H_2SO_4 persisted on the particles. Synergistic effects between other combustion-generated pollutants occurring on the same particle have been studied. For example, the combination of benzo[a]pyrene adsorbed on carbon black caused release of tumor necrosis factor-alpha and caused programmed cell death of lung macrophages, but neither carbon black nor benzo[a]pyrene had this effect alone.[316] Other synergistic effects involve particles plus a gas-phase pollutant, such as O_3.[320]

Importance of Chemically Speciated PM Sampling

Equal mass doses of sea salt, desert dust, and diesel exhaust are unlikely to have the same effect on the body. The startup of a large number of air monitoring sites that will routinely report individual chemical categories of PM (EC, OC, SO_4^{2-}, NO_3^-, other inorganic) and the funding of EPA particulate research centers and Supersites will provide input data for epidemiology studies. Improved characterization of combustion and other PM sources will provide data needed to relate the chemical speciation at receptor sites to the major sources. Controlled toxicology studies using exposure to well-characterized components

Table 9. Studies of ultrafine vs. larger particles of the same substance.

Material	Dose/Method	References	Results
Titanium dioxide 20-nm and 200-nm	Rat, instillation	331	Increased pulmonary toxicity of ultrafines related to surface area and the ability to enter interstitial spaces. Alveolar macrophage involvement.
Titanium dioxide 20-nm and 250-nm	Rat, inhalation, 22 mg/m^3, 6 hr/day for 6 months	410	Greater inflammatory response at equal dose with 20-nm particles.
Titanium dioxide 21-nm and 120-nm	Rat explants in vitro	411	Ultrafine particles were able to induce procollagen expression, which is related to development of airway fibrosis.
Carbon black 14-nm and 260-nm	Rat, instillation	329	Ultrafine carbon black had greater ability to produce lung inflammation at low dose.
Carbon black 14-nm and 260-nm	Rat, inhalation 1 mg/m^3, 7 hr one-time	319	No effect with 260-nm particles. Ultrafine produced proinflammatory response, oxidative stress, increased procoagulant blood factor.
Magnesium dioxide UF, 28% < 0.1 μm F, 98% < 2.5 μm	Human, inhalation	409	No significant differences in bronchoalveolar lavage cell concentration or cytokine concentration. Suggested that particle composition, not size alone, is significant.

of ambient aerosol will be needed to develop a mechanistic understanding of how particles affect the body.

AIR QUALITY REGULATIONS

The preceding discussion of the respiratory system and air pollution health effects sets the framework for discussing air quality regulations. These regulations have the primary purpose of protecting human health and the secondary purpose of reducing other environmental impacts of pollution. Environmental laws must be unambiguous for the regulated sources, the enforcement agencies, and the affected public. A prerequisite to developing a rule is that a means must exist to measure the component(s) to be regulated so that compliance monitoring can take place. This monitoring must be cost-effective and reproducible. As a result, the existing regulations focus on regulating ambient concentrations of pollutants for which reasonable cost, robust, and precise measurement methods are available.

Three sections of the U.S. Clean Air Act apply directly to PM. The most important of these are the NAAQS, which include PM_{10} and the newly implemented $PM_{2.5}$ regulations. The EPA[301] has indicated that the PM_{10} trend is improving, with a decrease of 26% in average ambient concentrations from 1988 to 1997. In 1987, the original NAAQS for total suspended PM was replaced by a PM_{10} standard set at 150 μg/m^3 24-hr average and 50 μg/m^3 annual average. The legal requirement to periodically review the standards, combined with growing epidemiologic evidence and a citizen lawsuit, lead to further rulemaking. In 1997, the EPA revised its existing PM standards by adding the $PM_{2.5}$ standard.[414] The annual standard is set at 15 μg/m^3, with a new 24-hr standard set at 65 μg/m^3. The PM_{10} annual standard was retained, but the statistical method of determining compliance with the 24-hr average was modified. The scientific evidence considered by the EPA in setting the standard was compiled into a criteria document.[305]

It should be noted that the standard was recently (May 14, 1999) challenged, and a panel of the U.S. Court of Appeals for the District of Columbia remanded the new standards for $PM_{2.5}$ and O_3. In a summary of the decision, the EPA points out that the court did not question the health evidence for the standard; rather, the decision required more explanation of the process used to set the standard. Congress has required the National Research Council to form a committee to guide the PM research and monitoring agenda. This committee is charged to write four reports between 1998 and 2002, when EPA is to complete a 5-year scientific review of the standards, leading to possible revision. Two of the four reports have been completed.[415,416] The current regulation is based on $PM_{2.5}$ measured by the Federal Reference Method. This mass is dominated by secondary SO_4^{2-} and NO_3^- aerosol and by EC and OC. Submicron inorganic ash and ultrafines from combustion are a small part of the $PM_{2.5}$ mass in many locations. However, the mass measurements do not directly relate to the previously discussed mechanistic toxicological hypotheses. Other characteristics, such as the morphology and chemistry of ultrafine particles, may be more important than

simple mass. The EPA is attempting to address this fact by its ambitious Supersite program. These Supersites intend to support the on-going health studies by obtaining chemical- and time-resolved data using a range of research methods. However, one must realize that cost-effective, robust, and simple monitoring methods must be available before any change in the present standards can be realistically promulgated and implemented.

The second regulation can be found in the regional haze rule.[417] Decreased visibility occurs due to the scattering and absorption of light by particles. This is of particular concern in the 156 National Parks and Wilderness Areas that are designated as mandatory Class I air quality areas in the United States. Since fine particles are transported over hundreds of miles, all 50 states will have to participate in planning, analysis, and, in some cases, emission control programs. Since submicron particles scatter light efficiently, combustion-generated PM has a large impact on visibility, even when the primary combustion PM represents a small part of the total $PM_{2.5}$ mass. The EC, which results in light absorption rather than light scattering, is particularly important for visibility. In addition, secondary PM, not covered by this review, is important. Regulations to control acid rain precursors and photochemical smog precursors also reduce the ambient particle concentration, since SO_2 and NO_x are also the precursors of secondary SO_4^{2-} and NO_3^- particles. Visibility rules may prove to be more stringent than health standards in controlling the emission of submicron particles from combustion sources.

Finally, the Clean Air Act Amendments of 1990 require the EPA to address 188 hazardous air pollutants (HAPs). Included in this list are As, Be, Cd, Co, Cr, Hg, Ni, Mn, Pb, Sb, and Se, which are contained in fuels. The accumulation of toxic metals, such as Se and Hg, and the accumulation of persistent organic compounds, such as chlorinated dioxins and furans, in ecosystems is a concern that affects standards for combustion particle emissions. Current regulations focus on sources emitting greater than 25 tons/year, and electric utility steam-generating boilers are temporally exempt from the regulations. Due to amplification in the food chain, and to public concern for wildlife and endangered species, these indirect effects of particles may also result in more stringent regulation of sources. Complying with the ecological goals of the HAP regulations will require an understanding of the relationship between combustion conditions and the emissions of these trace elements.

Adverse health effects originally identified by epidemiology studies motivated the public perceptions and legal actions that have resulted in new regulations for ambient PM. Current air quality standards are based on the mass of particles smaller than a specified size; however, toxicological studies may eventually identify specific categories of ambient PM that need stricter control to protect public health. Advances in understanding the formation and transformation of combustion aerosols and advanced monitoring techniques must take place to meet the challenge of setting and complying with regulatory standards.

TIME- AND SIZE-RESOLVED PARTICLE MEASUREMENTS

The ability to test various health-related hypotheses is closely linked to which PM characteristics can be measured at combustion sources and in the ambient air. The particle measurement issues that are especially relevant for testing current health effects hypotheses regarding metals, ultrafines, and soot from combustion sources include

- *Measurement Artifacts*. This includes all the particle transformations that can be different between a sampling train and the ambient air. Due to the effects of temperature-dilution history on the partitioning of chemical species between the gas phase and the particles, the PM that is measured in the laboratory may have a different size-dependent composition than the PM to which the population is exposed. Also, transformation of the particle size distribution due to coagulation, surface condensation, chemical reactions, and size-selective removal may occur as a result of the sampling methodology.
- *Instrument Limitations*. Methods are needed to measure particle-to-particle variation, which provides information that is lost in the bulk average properties of the PM collected by filter sampling. Rapid response instruments are needed to quantify short duration transients in particulate air pollution that may have significant health effects. Many methods for measuring aerosols that were developed for supermicron particles need to be modified or extended for ultrafine PM.

Measurement Artifacts

The historic regulation of the total PM mass smaller than a given size has produced precise mass measurement techniques. Since the largest particles dominate the mass, there has been an emphasis on isokinetic sampling. There has also been concern about equilibrating the samples to constant humidity before weighing, even though the mass of particle-bound water is unlikely to have biological importance. The techniques that yield precise mass measurements may, however, introduce serious artifacts if the goal is to obtain data on submicron particle composition and size distribution. For example, allowing air of variable temperature, pollutant concentration, and humidity to pass over the accumulating filter deposit for 1–6 days can strip

the more volatile species from the collected particles before the sample is weighed. This has led to the development of samplers that can quantify the volatile PM.[418,419] While there is uncertainty regarding the significance of the mass of volatiles adsorbed on particles, this serves as an example of the importance of using appropriate particle measurement methods when testing a given toxicological hypothesis.

Condensable PM, that is, material that condenses into a liquid or solid within a few seconds of leaving the stack, can be comparable in mass to the filterable PM_{10} measured in the stack of a power plant.[420] Currently, U.S. regulations do not require measuring condensable PM when stack-testing stationary sources. This is another example of how measurement protocols developed for regulatory compliance do not collect the data that is most needed for health and environmental studies.

Dilution tunnels were developed for measuring condensable particulate, including both SO_4^{2-} aerosol and organic compounds from vehicle exhaust and stationary sources of VOCs.[278,421] The dilution tunnel process involves mixing the hot combustion emissions with filtered air, allowing a short residence time, then extracting a particulate sample for either on-line analysis or for collection on a filter. Dilution tunnels were developed to measure mass and chemical composition of PM. The possibility that a laboratory dilution tunnel could create a different particle size distribution than the size distribution that occurs during natural dilution was pointed out by Kittelson and Dolan 20 years ago.[422] Since then, many papers have discussed the artifacts that can occur in dilution tunnels.[265,423–428]

The formation of particles during dilution depends on the opposing effects on condensation of the decreasing saturation pressure of the volatile species due to cooling and the decreasing partial pressure of the volatile species due to mixing. The saturation reaches a peak in the dilution range of 5:1 to 50:1, depending on the boiling point of the volatile species and the initial temperatures of the exhaust and dilution gases. Particles will be formed by nucleation if the mixture stays in this dilution range for sufficient time for significant mass transfer to take place. Typical dilution tunnels operate in the range of 3:1 to 20:1 and have residence times on the order of seconds, so critical supersaturation may be exceeded long enough for formation of nuclei particles followed by rapid growth from condensation. The formation of H_2SO_4/H_2O particles is an example in which dilution conditions influence the measured particle number both in dilution tunnels[429] and in the atmosphere.[430]

Unlike mass, particle number is not conserved, and the effect of dilution conditions makes it difficult to compare the particle number size distributions measured by different investigators. This is especially important when using combustion source measurements for investigating the health effects of ultrafines and nanoparticles. Changes in particle number of up to 2 orders of magnitude have been reported when conditions were varied over the typical range used in laboratory dilution systems.[429] Initial combustion exhaust conditions, dilution history, dilution gas temperature and relative humidity, and the residence time interact to affect nucleation and surface growth. Careful interpretation of conditions used for experiments is required. For example, diesel exhaust studies have reported that high dilution ratio both increases[426] and decreases[429] formation of particles below 50 nm.

Research studies of the particulate emissions from IC engines fall into two groups: studies of the transient mixing and chemical reactions inside the cylinder, and studies of the tailpipe emissions to the atmosphere. Between these points is the exhaust system in which the undiluted exhaust cools and ages, but is not diluted. The gas residence time in the engine cylinder is 10–30 msec, depending on engine speed. The time from the cylinder to the atmosphere for a typical heavy-duty truck engine exhaust system is 100–300 msec, about 10 times greater. The extractive particle sampling systems used by various investigators can add another 0.25–1 sec or more to the age of the aerosol before dilution begins. The dilution of tailpipe exhaust under highway conditions starts at the tailpipe and is about 1000:1 after 1 sec.[423] The coagulation of equal size particles is proportional to n^2, so most particle growth by coagulation takes place prior to the onset of exhaust dilution. Under urban conditions, once combustion exhaust is diluted more than ~100:1, the collisions between accumulation mode particles from the ambient air and ultrafines from the combustion source become significant compared with the coagulation between ultrafine particles originating from a single source.

The ultrafine particle size distribution formed from hot diesel exhaust in a laboratory dilution tunnel operating with filtered air may be very different from the size distribution formed under roadway dilution conditions with ambient air. Ambient air contains accumulation mode particles that, due to the increased collision rate between particles of different size, increase the rate at which the nuclei and condensation mode ultrafines are depleted. A novel approach to studying dilution effects involves the simultaneous use on a moving truck of both a dilution tunnel extracting from the tailpipe and an in-plume sampler with the inlet mounted on the rear of the trailer.[431] For these experiments, the dilution system measurement showed a smaller accumulation mode mean size than did the in-plume measurement.[432]

Nanoparticles are difficult to measure because they are rapidly transformed by coagulation, surface growth, and transport to the walls of the equipment. Internal

combustion engine particle number measurements may contain artifacts from the sampling lines due to both desorption of condensed material and reentrainment of deposits. A dynamometer study comparing tailpipe and dilution tunnel measurements of gasoline vehicle exhaust particle concentration found that a heated and insulated transfer line resulted in a very intense nanoparticle mode when the drive cycle involved operation at high vehicle speed.[433] This ultrafine mode was not detected under identical operating conditions with an unheated transfer line. This artifact was attributed to the hot exhaust increasing the transfer line temperature above 180–250 °C, resulting in desorption/pyrolysis of organic material in the line.

There is a need for improved technology for making laboratory measurements of combustion PM that can be related to the real behavior of particles in the combustor exhaust, the initial plume, and the atmosphere. Computer simulations of the fundamental mechanisms of aerosol formation and transformation can be used to interpret and compare particle size distribution data collected under various dilution configurations. Rapid dilution is essential if the ultrafines generated in combustion are to be measured. Likewise, ultrafines are most likely to survive from the combustion source to inhalation exposure when there is rapid dilution with relatively clean ambient air.

The commonly used instruments have limitations that may introduce artifacts into measurements of ultrafine particles. Many published graphs of combustion particle number distributions show the highest concentration in the smallest size range measured by an SMPS. This makes the integrated total particle number suspect since there may be extremely high concentrations of undetected nuclei particles present. Some authors explicitly acknowledge this measurement truncation problem by stating the results as the total number within the range of the SMPS. Another approach, for example, that used by Khalek et al.,[262] is to fit a lognormal distribution to the data with an algorithm that allows for truncated measurements. Truncation of the measured size distribution is an important issue both when using experimental data as the input to a coagulation model calculation and when testing toxicological hypotheses related to ultrafine particle number.

Characterization of particle number and chemical composition from combustion and other PM sources is important for both source apportionment studies of the submicron ambient aerosol and for designing controlled tests of particular toxicological hypotheses regarding ultrafines, metals, and synergistic effects between particle components. The size distribution measured from dilution tunnel sampling shows artificially high numbers of particles. However, there is also the possibility that a substantial portion of the nuclei is below the detection limit of the instruments used.

Instrumentation Needs

To understand what particle characteristics affect human health, we must develop ways to make inexpensive, robust measurements of particle size distribution, morphology, and chemical speciation. The important variables have not yet been identified, but the current inhalation toxicology research direction suggests that a better understanding of health effects will require more time-resolved, size-segregated, chemically speciated data from both combustion sources and ambient monitors. Testing of epidemiologic hypotheses requires wide-scale, long-term measurement of PM characteristics. The characteristics selected for measurement should be economical to quantify under field conditions and should be well correlated with the factors that are suspected to be biologically significant.

Filter samples provide only time-averaged aerosol properties, but individual particle composition contains information that is important for both source apportionment and toxicology studies. The urban aerosol contains contributions from nearby and regional sources, both natural and anthropogenic, that have aged in the atmosphere from minutes to days. A typical ambient particle that is inhaled consists of coagulated primary combustion particles or geological particles, coated with some mixture of condensable organic species, secondary SO_4^{2-} and NO_3^-, and H_2O at equilibrium with local humidity. The particle-to-particle variation reflects different sources and transformation histories. The different particle types within the ambient mixture are likely to have different effects when inhaled. The information on particle-to-particle variation is preserved by single particle techniques, such as electron microscopy and aerosol mass spectrometry. However, it is necessary to efficiently measure a statistically large population of particles to obtain meaningful ensemble averages of the ambient PM as a function of time and place.

The wide variation in the physical and chemical characteristics of combustion PM emissions as operating conditions change creates a need for near-real-time measurements that can capture both the transient emissions and the variation between individual sources in a category. For IC engines, toxicological hypotheses motivate a desire to characterize the soot, the soluble organic compounds including individual PAH, the ultrafine particle number, and the metal speciation with various fuels at various speeds and loads. Likewise, measurements of a few boilers, gas turbines, or fireplaces cannot be expected to fully describe the emissions from all similar sources. One of the most challenging combustion PM problems is

to characterize highly variable sources such as open burning and domestic biomass combustion. Compliance monitoring methods such as filter sampling of an automobile over the FTP drive cycle, or a 2- to 4-hr steady-state stack test of a boiler, cannot measure the transients. Collecting statistical data on a representative sample of in-service sources is slow and very expensive using compliance methods. This section will discuss some of the research instruments that may offer improved capability to make time- and size-resolved measurements of $PM_{2.5}$ and ultrafine PM.

Desirable instrument characteristics for testing epidemiologic hypotheses include low cost per data point to allow collection of sufficient data to perform statistical analysis, rapid response to allow tracking of transients, reliability and ruggedness to allow use under field conditions, and reproducibility to allow comparisons between investigators. Desirable characteristics for source apportionment and toxicology studies are the ability to provide information on detailed morphology and chemical composition that is relevant to the origin of the particle and its behavior inside the body.

Chemical analysis techniques for source apportionment rely on variation in the concentration of specific compounds that provide individual "markers" or "fingerprints" (i.e., characteristic patterns) for identification of sources. The pioneering studies used elemental composition: Pb for gasoline engines, V for oil-burning power plants, Se for coal-fired boilers, and Al for geological materials.[306] This allowed identification of only a few categories, and changes in technology, such as the phase-out of leaded gasoline, have eliminated some of the markers. Compared with less than 50 elements that are potential markers of combustion particles, organic compounds provide tens of thousands of potential markers, allowing detailed identification of combustion sources.[156,298,434,435] A "memory" of the original fuel is preserved in the detailed composition of the products of incomplete combustion. A limitation of these organic markers is the time needed to collect and analyze a sample by conventional solvent-extraction and gas chromatography. An alternative technique, currently being tested in research programs, is thermal desorption gas chromatography (TD-GC),[436] which involves controlled heating of a lightly loaded particulate filter. This method has been shown to provide composition data with 2-hr time resolution that are nearly identical to collocated 24-hr samples that were analyzed by conventional solvent-extraction, GC/MS methods. Prototypes indicate that TD-GC has the potential to be fully automated in a field-transportable unit.

Another option for rapid organic analysis is the photoelectric aerosol sensor (PAS),[437,438] which provides a real-time indication of changes in the amount of particle-bound PAH. This instrument is compact and has a sensitivity of about 1 ng PAH/m^3.[439] The value of rapid time-resolved PAH measurement is illustrated by a study in which a PAS was installed near the runway of an Air Force base. The spikes in the signal could be correlated with flight logs showing the activity of specific aircraft, as indicated in Figure 19.[440] The PAS signal is a weighted sum from many chemical species. Some research has been completed to quantify the relationship between the PAS instrument reading and conventional measurements of individual PAH by traditional methods for a range of sources. The ability to make rapid semi-quantitative measurements of PAH is extremely valuable for characterization of the variation in the emissions from large populations of similar sources, and to study the effect of combustion transients on the time-averaged emissions. Ongoing research includes developing methods to use the PAS to monitor for high PM-emitting equipment in an operational fleet through edge-of-roadway or edge-of-runway real-time measurements.

Soot is a functional definition and actual combustion particulate emissions are a complex mixture of organic compounds ranging from unburned fuel to graphite-like polycyclic structures, making an arbitrary division into composition categories necessary. These divisions are based on behavior in an analytical procedure. The measured split between OC and EC is based on the light-adsorbing properties of a filter punch as a function of temperature, first under a helium atmosphere and then under an oxygen/helium atmosphere.[441] Changes in the procedure, for example, the NIOSH and IMPROVE methods, give different results.[442] The fuel- and lubricant-derived hydrocarbons are alternatively distinguished from the graphite-like carbon structures in soot by measuring the soluble organic fraction using dichloromethane or a similar solvent.[443] Further separation of the soluble organic compounds usually involves extraction with aqueous and organic solvents, acidic and basic solvents, and polar and non-polar solvents until various classes such as paraffins, aromatics, and oxygenates are isolated for analysis by gas chromatography.[275,276,444,445]

EC, or soot, is an important class of particulate air pollution, and the ability to economically make near-real-time measurements of EC is valuable for characterizing transient emissions from combustion sources. The photoacoustic analyzer detects light-absorbing particles (black carbon) by the transient heating resulting from a pulsating laser beam passing through the sample chamber.[446,447] A preliminary study of IC engine exhaust showed that the photoacoustic instrument response and the EC analyzed on filter samples by thermal/optical reflectance[441] correlated as shown in Figure 20.[448] This technique provides a rapid signal, making time-resolved measurements of events, such as sudden acceleration of

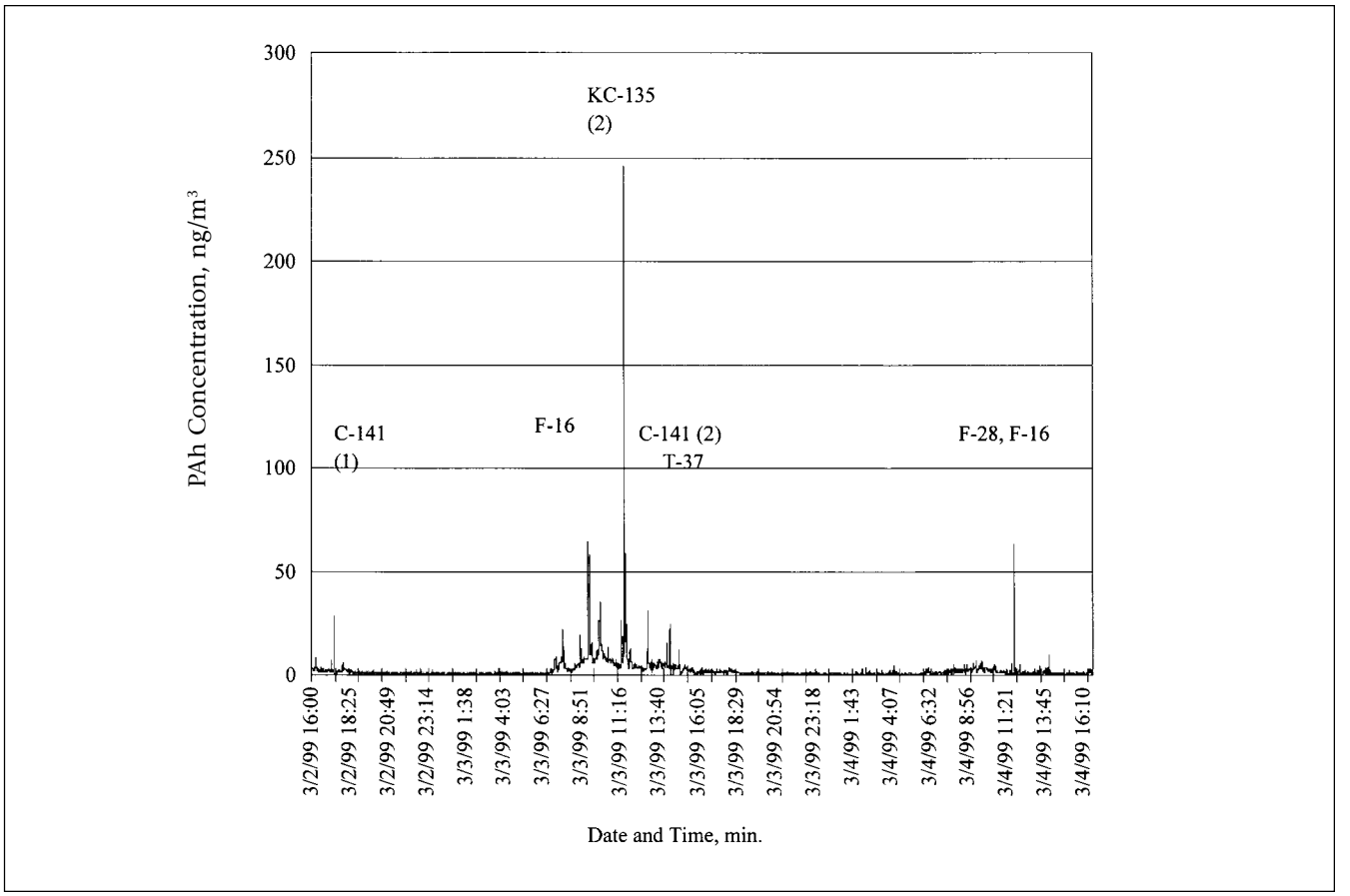

Figure 19. Time-trend data obtained by a PAS sampling at an Air Force base. The spikes in PAH concentration can be correlated with aircraft operations and with local ground traffic. Courtesy of G. Palmer.[440]

the engine, feasible. The instrument also has a wide dynamic range, making it suitable both for studies of transient emissions from combustion sources and for monitoring spikes in ambient concentration. The lower limit of detection for EC is 40 ng/m^3.[447] When developing alternative methods for measuring the health and visibility impacts of soot and of particle-bound organics, there is a need to compare these methods to existing EC and OC data. However, EC, as currently reported, is a method-dependent definition, so the relationship between methods is only an empirical correlation, not a fundamental relationship.

Electron microscopy, coupled with energy dispersive X-ray analysis, can provide size, shape, and elemental composition information on individual particles. Automated electron microscopy, also called CCSEM, allows the characterization of several hundred particles per hour and provides a powerful technique for characterizing both source and receptor samples for source apportionment studies.[449,450]

Concern over acid rain has motivated studies that have looked for coal particles in lake sediments as a tracer for rain-out from power-plant plumes. The methods used to identify coal fly ash in sediments can also be extended to plume tracking for health studies. An early example of using CCSEM in a health-related combustion particle study involved collecting particles from the plume of a coal-fired power plant using a helicopter. Kim et al.[451] showed that the plume particles could be distinguished from background PM by the characteristic morphology and composition of coal fly ash. Characteristics of combustion ash include large carbonaceous spheroidal particles[452] and glassy aluminosilicate spheres.[453,454] Advanced techniques for single particle analysis by microscopy have been reviewed.[455,456] A limitation to the study of submicron particles is that the spatial resolution of many techniques, such as energy-dispersive X-ray analysis, is comparable to the size of the particles.

The aerosol time-of-flight mass spectrometer (ATOFMS) is the most sensitive technique currently available for on-line measurement of the size and chemical composition, both organic and inorganic, of individual aerosol particles. The size and chemical composition of hundreds of particles per minute can be obtained. Fundamentals of the ATOFMS technique and recent advances in aerosol mass spectrometry are discussed in a review,[457] which lists the contributions of 17 research groups. Figure 21 illustrates the capabilities of an ATOFMS research

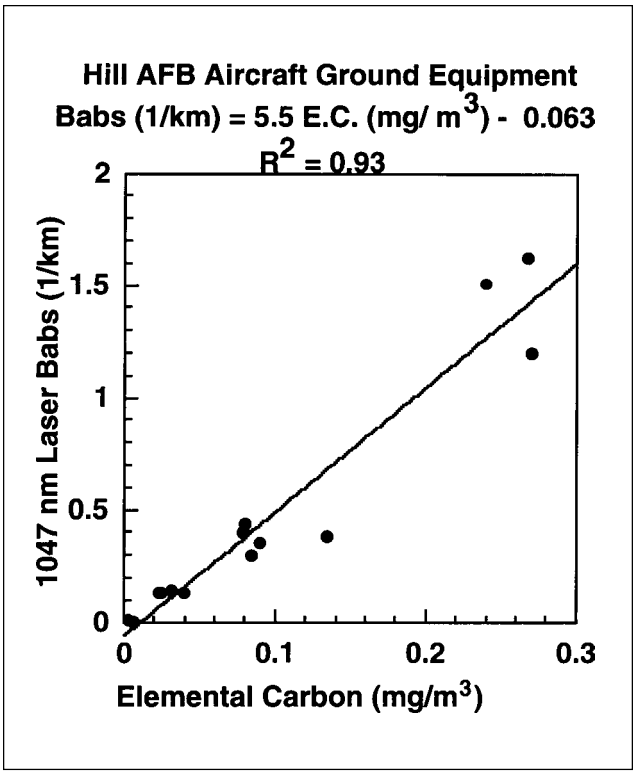

Figure 20. Comparison of near-real-time light absorption measured by the photoacoustic analyzer (PA) and EC measured by thermal-optical reflectance (TOR) of filter samples.[448] The two techniques show good correlation for a range of IC engine sources. Courtesy of P. Arnott.

instrument similar to a design that is now commercially available. Studies have compared the composition of source PM and of ambient PM by cascade impactor time-averaged samples and by time trend data from the ATOFMS.[458] Real-time characterization of aerosol time-of-flight mass spectroscopy has also been used in studies of diesel exhaust to study PAH composition under various operating conditions.[459]

Figure 21 illustrates four single particle mass spectra sampled using an on-line single particle mass spectrometer developed at the University of California, Riverside.[457,460] These four single particles are representative of (a) diesel- and (b) gasoline-powered vehicular OC-containing particulate emissions, (c) coal combustion, and (d) ambient dust. Figures 21a–c show single particles collected during controlled source characterization studies utilizing a dilution sampler.[276,278] These illustrate how single particle source characterization studies allow for the identification and differentiation of PM sources. Figures 21a-1 and 21a-2 are the cation and anion spectra, respectively, of an OC-containing particulate emitted from a 1994 Ford E350 diesel truck. The cation spectrum contains many low mass organic fragments, as well as nitrogen-containing species. Peaks of interest from the cation spectrum include m/z 12 (C^+), m/z 18 (NH_4^+), m/z 27 ($C_2H_3^+$), m/z 43 ($C_3H_7^+$, $C_2H_3O^+$, $CHNO^+$) m/z 86, and m/z 101. The

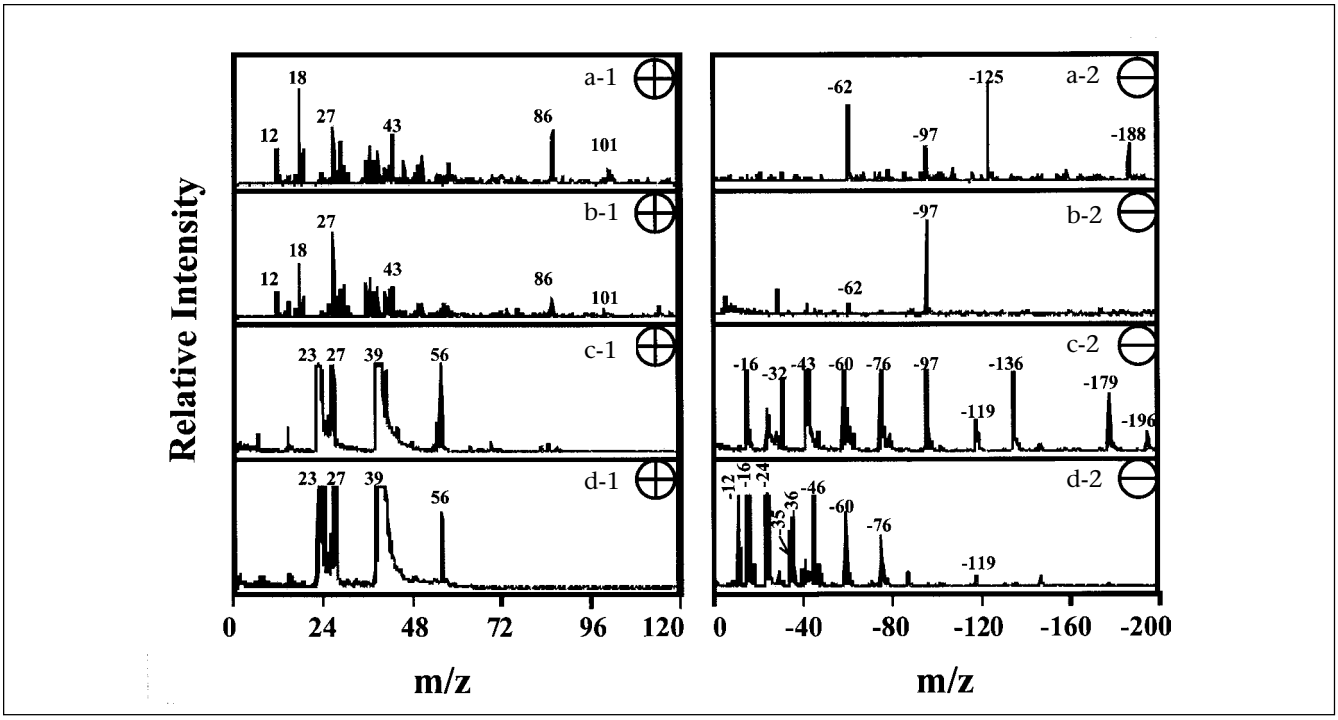

Figure 21. Mass spectra from four different single aerosol particles. a-1 through d-1 are single particle cation spectra and a-2 through d-2 are their associated anion spectra. a-1 and a-2 are from a single particle emitted from a diesel-powered 1994 Ford E350 truck. b-1 and b-2 represent a single particle emitted from a gasoline-powered 1993 Honda Civic. c-1 and c-2 represent a single particle emitted from the combustion of Illinois coal. d-1 and d-2 represent an ambient Riverside, CA, dust particle collected on Oct. 7, 1999. Each of these single particles is representative of its specific source or type. Courtesy of K. Prather and D. Suess.

anion spectrum contains fewer signals, and these are dominated by sulfur- and nitrogen-containing species including m/z –62 (NO_3^-), m/z –97 (HSO_4^-), m/z –125 ($HN_2O_6^-$) and m/z –188 ($H_2N_3O_9^-$).

Figures 21b-1 and 21b-2 are representative OC-containing single particles emitted from a gasoline-powered 1993 Honda Civic. The cation spectrum, Figure 21b-1, contains very similar low-mass organic fragments to those observed from the diesel-powered vehicle, 21a-1. Therefore, differentiating OC-containing single particles from gasoline- and diesel-powered vehicles solely by their positive spectra is not possible. However, with additional information from the anion spectra, these OC-containing single particles can be differentiated. Figure 21b-2 does not contain signals at m/z –125 or m/z –188. As shown in Figure 21a-2, signals at these m/z values are associated with diesel-powered OC vehicular emissions.

Figures 21c-1 and 21c-2 are representative Illinois coal combustion. The cation spectrum contains signals at m/z 23 (Na^+), m/z 27 (Al^+), m/z 39 (K^+) and m/z 56 (Fe^+). In contrast to Figures 21a and b, the complexity of this inorganic particle type lies in the anion spectrum. Chemical species present in Figure 21c-2 include m/z –16 (O_2^-), m/z –32 (S^-, O_2^-), m/z –43 (BO_2^-), m/z –60 (SiO_2^-), m/z –76 (SiO_3^-), m/z –97 (HSO_4^-), m/z –119 ($AlSiO_4^-$), m/z –136 ($Si_2O_5^-$), m/z –179 ($AlSi_2O_6^-$), and m/z –196 ($Si_3O_7^-$). Figures 21d-1 and 21d-2 represent an ambient dust particle sampled in Riverside, CA, on October 7, 1999. The cation ambient dust spectrum is indistinguishable from the coal combustion single particle cation spectrum in Figure 21c-1, but the anion spectra allow for differentiation between these single particle types. Signals in Figure 21d-2 differing from Figure 21c-2 include m/z –12 (C^-), m/z –24 (C_2^-), m/z –35 (Cl^-), m/z –36 (C_3^-), and m/z –46 (NO_2^-). Interestingly, the sulfur-containing species are absent from the ambient dust single particle, as well as from higher mass silicate clusters.

As more single particle source characterization studies are performed, the goal of performing source apportionment of ambient aerosols on a single particle basis becomes more feasible. Data such as these illustrate that it should be possible to distinguish vehicle emission particles from different engine types from other combustion processes such as coal. In addition, the differentiation of coal from ambient dust should be possible using the unique combination of ion markers shown here.

The ATOFMS measurements of single particle composition can provide data on the variation in both source and ambient particles that is lost in filter samples. This allows detailed characterization of both combustion sources and ambient particles on a level of detail that will be suitable for testing of specific toxicological hypotheses; however, this technique has limitations. Large particles are preferentially detected by the ATOFMS, which requires correcting the raw data for the counting efficiency.[461] The current limit of detection is ~0.2 μm. Work is on-going to extend the capability of this technology to characterize ultrafines and nanoparticles.

Both source-based modeling and ambient studies with real-time instruments have demonstrated that the composition of the ambient aerosol has short-term variation as the wind brings in particles from various mixtures of sources. Presently, the relative importance of time-averaged exposure versus short-term exposure to spikes in the ambient aerosol composition is unknown. Some laboratory studies have shown strong responses from short exposures to high particle concentrations.[462] Figure 22 shows the time-resolved PM_{10} and $PM_{2.5}$ measured at an active military base located near an urban area.[440] These transients are suspected to result from nearby sources. The ATOFMS, PAS, and photoacoustic analyzer and similar near-real time instruments provide the analytical tools needed to begin testing hypotheses related to transient exposure. Advances in both data reduction capability and in instrumentation capability, especially with regard to the submicron and nanoparticle components, are still needed.

CONCLUDING COMMENTS

Providing the scientific basis for improved regulation of the emission of combustion particles requires an interdisciplinary approach with interactions between researchers in combustion, air pollution control, atmospheric transport and transformation, exposure assessment, and health effects, together with the regulatory community. The review has touched briefly on relevant information in these areas, providing references for the reader interested in more detailed coverage. Gaps exist in the scientific understanding of all elements of the problem, but the greatest gaps are at the interfaces between the fields. In addition to the need to fill these gaps, there is a need for a better balance between applying the knowledge that has been gained to answer pressing questions and refining the theory to gain better solutions. Significant progress has been made in understanding the processes governing combustion particle formation:

- Particles emitted from combustors are either generated by condensation or, in the case of soot, molecular weight growth reactions that lead to the formation from the gas phase of submicron aggregates of primary particles. Significant progress has been made in understanding the factors controlling the amount, size, and composition of these submicron particles. Their mass is determined primarily in the early stages of combustion for soot, inorganic ash, and condensable hydrocarbons. H_2SO_4 is controlled by

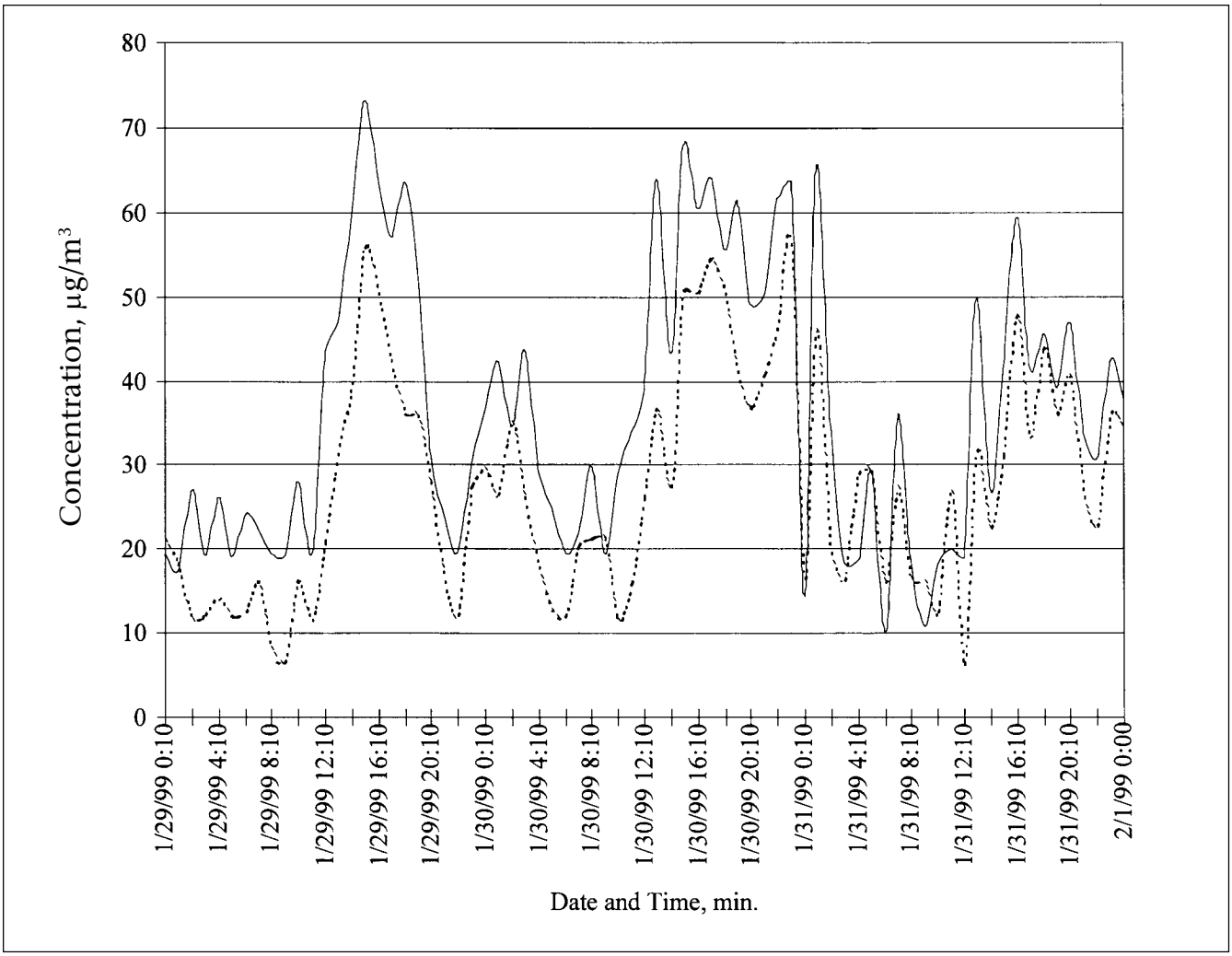

Figure 22. Time trend measurements of PM_{10}(——)and $PM_{2.5}$(------) by a beta attenuation meter show short-term spikes in fine particles, presumably from nearby combustion sources. Courtesy of G. Palmer.[440]

the oxidation of SO_2, primarily catalytically, on tube surfaces, fly ash, and, for certain vehicles, catalytic converters. The number and size distribution of the aggregates is controlled by collision and coagulation processes that are relatively well understood.

- Supramicron combustion-generated particles are produced by the agglomeration of the mineral content in fuels and by the coking of heavy hydrocarbons in fuel oils or coals. The size of these particles is, to an order of magnitude, equal to that of the parent fuel particles for pulverized or atomized fuels. The larger particles will be emitted only in the case of combustion systems not equipped with particulate control equipment. Large particles of carbonaceous material are also important for uncontrolled combustors such as fireplaces and open burning.
- Trace, sometimes toxic, elements are emitted in small enough amounts not to contribute significantly to the mass of the emitted particles. They are distributed between the sub- and supramicron particles emitted by combustors by condensation and surface reaction, sometimes modified by diffusion through pores. The processes governing the distribution of the trace elements are relatively well known; the size dependence of the concentration depends on the controlling mechanism and can provide a means for determining that mechanism.

The particle formation mechanisms have been used mainly in interpreting laboratory data. Although imperfect, they are at a stage where they can be incorporated in computational fluid dynamics simulations of furnaces and boilers to make predictive calculations of the particle size distribution and composition. In order to predict emissions, one needs to combine the information on the size and composition distribution of the particles emerging from combustors with information on the collection efficiency of the APCDs. The penetration of the APCD by

particles will vary with the design and operation of the APCD. No control devices are installed on many small combustors or combustors operated with clean fuels, so that the emissions are closely approximated by the combustion emissions.

The limited studies of the PM at the inlet and outlet of APCD devices on full-scale combustion systems show that particle penetration is greatest in the 0.1–1.0 μm range, that is, in the transition of dominance of inertial forces to particle diffusion. There is a need to integrate models of the APCD with those of particle formation. At present, the greatest investment in the measurement of particle emissions has been carried out for compliance purposes and provides data on the total (not size-dependent) penetration efficiency of different elements. Without a mechanistic model, it is not possible to determine how these emission parameters change with changes in fuel, combustion conditions, or the operation and maintenance of the APCD. Further, little effort has been directed at extending the knowledge gained from studies of particle formation in engineered combustion chambers to some of the more mundane sources, such as domestic combustion and open burning. These types of sources are of increasing environmental importance as the emissions from boilers, furnaces, and IC engines become better controlled through improved technology.

Empirical emission factors become quickly dated as regulations are tightened, and as technological changes impact fuel composition and combustor design. The trends in emissions for major combustion sources show decreasing total mass emissions from coal-fired and oil-fired boilers and from on-road diesel engines. Modifications of older stationary sources and the retirement of older vehicles have more than offset the increases due to growing population and economic activity. More attention needs to be focused on biomass sources if these are used to significantly supplant fossil fuel combustors. A major question, however, arises as to whether decrease in mass emission per se achieves the desired impacts of safeguarding human health, since in many cases, the decrease in mass is accompanied by an increase in numbers of smaller particles.

Examination of the size and composition of combustion-generated particles shows that, compared with geologically generated ambient PM, they are smaller and have unique chemical composition and morphology that reflect the fuel composition, the combustion conditions, and the particle transformations between the furnace and the stack. The data generated for compliance purposes provide a starting point, but are not adequate to answer many of the health-related hypotheses being proposed. More characterization studies will be needed for particle sources, including measurements of transient emissions, detailed chemical speciation, and ultrafine particle number. The complex aerosol mixture produced by combustion is further transformed in the atmosphere before human exposure by mechanisms that, though subject to uncertainty, are sufficiently well understood to provide reasonable models of ambient particles from well-characterized emissions.

Epidemiology has demonstrated that susceptible individuals are being harmed by ambient particulate air pollution at levels comparable to the current air quality standards. Based on these findings, new regulations have been proposed for $PM_{2.5}$, but these have been contested. The proposed regulations based on mass loading are to be subject to review as current research leads to better understanding of the mechanism for the health impact of particles and of which specific size fractions and chemicals are responsible for these effects. Controlled studies with surrogate particles are being conducted to help unravel the various hypotheses proposed for the biological effects associated with the exposure to ambient particles. The problem is confounded by the probability that different particle characteristics are associated with different health end points in different susceptible populations. Particle surface area, number of ultrafine particles, and bioavailable transition metals are likely to be found to be more important than particle mass when correlating health effects with air pollution.

The understanding of the effects of particle air pollution on health has benefited from great advances in biochemistry and molecular biology on one side and from improved particle measurement capabilities on the other. Mechanistic toxicology studies are currently looking at the activation of specific genes and the synthesis of specific proteins in response to exposure to particles. Advances in the ability to collect time- and size-resolved research data on the composition of the ambient air will provide valuable input data for health studies and help identify the particle characteristics that are actually responsible for biological responses.

As the particles of importance to human health are identified, time- and size-resolved data will be needed for source apportionment studies both during the development of plans to improve air quality, and for the development of particle-control engineering technology for stationary and mobile sources. The health effects and apportionment studies can be assisted by the knowledge derived from the more fundamental studies on how fuel and combustion conditions affect size and composition of particulate emissions.

The observed association of increased ambient PM with adverse health effects and the lack of a toxicological mechanism provide the dilemma of balancing the added

Table 10. Nomenclature.

APCD	Air pollution control device
ATOFMS	Aerosol time-of-flight mass spectrometer
D_p	Aerodynamic or physical diameter of a particle
EC/OC	Elemental carbon and organic carbon, respectively, as measured by thermal/optical reflectance or a similar method
ESP	Electrostatic precipitator
EPA	United States Environmental Protection Agency
f_v	Volume fraction of a species (metal oxide or soot) per volume of gas
GC	Gas chromatograph
NAAQS	National Ambient Air Quality Standards
PAH	Polycyclic aromatic hydrocarbons
PM	Airborne particulate matter
SMPS	Scanning mobility particle sizer

cost to society of implementing imperfect regulations against the health costs of delaying action. The role of epidemiology during the 1854 cholera outbreak in London is instructive.[463] Dr. John Snow showed a correlation between cholera deaths and water from the Broad Street pump. Discovery of the germ theory of disease by Louis Pasteur was still 11 years in the future, and isolation of the cholera bacteria was 32 years in the future.[464] However, closing the well, based solely on associations and in the absence of a biological mechanism, stopped the epidemic and saved lives. Implementing a stricter fine particle standard can be seen as an analogous to "removing the pump handle." However, closing the offending well had a small cost, since other sources of water were nearby. Major reductions in the emissions of primary particles, especially ultrafines, from stationary and mobile combustion sources will require both advances in engineering practice and major investments of capital.

The cost of the implementation of the regulations can, however, be reduced by contributions provided by advances in the fields of aerosol and combustion science, combined with advances in biochemistry and toxicology. A causal relationship between ambient particles from different sources and specific health end points is needed to provide a sound scientific basis for regulations. These scientific contributions will eventually allow better prioritization of air pollution control resources. The tradeoffs between social costs and health risks are value judgments that need to be resolved through the political process, but that process can be assisted by the clarification of the scientific issues.

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REFERENCES

1. Mauderly, J.L. Summary of the Third Colloquium on Particulate Air Pollution and Human Health, Durham, North Carolina, June 6-8, 1999. In *Third Colloquium on Particulate Air Pollution and Human Health, Durham, North Carolina*; Air Pollution Health Effects Laboratory: University of California, Irvine, 1999; pp 3-9–3-14.
2. Glovsky, M.M.; Miguel, A.G.; Cass, G.R. Particulate Air Pollution: Possible Relevance in Asthma; *Allergy Asthma Proc.* **1997**, *18(3)*, 163-166.
3. Mauderly, J.L. Toxicological Approaches to Complex Mixtures; *Environ. Health Perspect.* **1993**, *101(Suppl. 4)*, 155-165.
4. Albritton, D.; Greenbaum, D.S. Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter. In *PM Measurements Research Workshop;* Health Effects Institute: Chapel Hill, NC, 1998; pp 9-12.
5. Mauderly, J.; Neas, L.; Schlesinger, R. PM Monitoring Needs Related to Health Effects. In *Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter;* PM Measurements Research Workshop; Health Effects Institute: Chapel Hill NC, 1998; pp 9-14.
6. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics—From Air Pollution to Climate Change*; Wiley: New York, 1998.
7. Finlayson-Pitts, B.J.; Pitts, J.N.J. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*; Academic Press: San Diego, CA, 2000.
8. Flagan, R.C.; Seinfeld, J.H. *Fundamentals of Air Pollution Engineering*; Prentice Hall: Englewood Cliffs, NJ, 1988.
9. Ulrich, G.D. Theory of Particle Formation and Growth in Oxide Synthesis Flames; *Combust. Sci. Technol.* **1971**, *4*, 47-57.
10. George, A.P.; Murley, R.D.; Place, E.R. The Formation of TiO_2 Aerosol from the Combustion Supported Reaction of $TiCl_4$ and O_2; *Faraday Symp. Chem. Soc.* **1973**, *7*, 63-71.
11. Oxtoby, D.W. Nucleation. In *Fundamentals of Inorganic Fluids;* Henderson, D., Ed.; Marcel Dekker: New York, 1992; pp 407-442.
12. Oxtoby, D.W. Homogeneous Nucleation: Theory and Experiment; *J. Phys.: Condens. Matter* **1992**, *4*, 7627-7650.
13. Mirabel, P.; Katz, J.L. Binary Homogeneous Nucleation as a Mechanism for the Formation of Aerosols; *J. Chem. Phys.* **1974**, *60*, 1138-1144.
14. Flagan, R.C.; Friedlander, S.K. Particle Formation in Pulverized Coal Combustion–A Review. In *Recent Developments in Aerosol Science;* Symposium on Aerosol Science and Technology, Atlantic City, NJ, August 1976; Shaw, D.T., Ed.; Wiley: New York, 1976; pp 25-59.
15. McNallan, M.J.; Yurek, G.J.; Elliott, J.F. The Formation of Inorganic Particulates by Homogeneous Nucleation in Gases Produced by the Combustion of Coal; *Combust. Flame* **1981**, *42*, 45-60.
16. McLean, W.J.; Hardesty, D.R.; Pohl, J.H. Direct Observations of Devolatilizing Pulverized Coal Particles in a Combustion Environment. In *18th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1981; pp 1239-1248.
17. Seeker, W.R.; Samuelsen, G.S.; Heap, M.P.; Trolinger, J.D. The Thermal Decomposition of Pulverized Coal Particles. In *18th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1981; pp 1213-1226.
18. Timothy, L.D.; Froelich, D.; Sarofim, A.F.; Béer, J.M. Soot Formation and Burnout During the Combustion of Dispersed Pulverized Coal Particles. In *21st Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1986; pp 1141-1148.
19. Helble, J.; Neville, M.; Sarofim, A.F. Aggregate Formation from Vaporized Ash during Pulverized Coal Combustion. In *21st Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1986; pp 411-417.

20. Helble, J.J.; Sarofim, A.F. Factors Determining the Primary Particle Size of Flame-Generated Inorganic Aerosols; *J. Colloid Interface Sci.* **1989**, *128(2)*, 348-362.
21. Neville, M.; Sarofim, A.F. The Stratified Composition of Inorganic Submicron Particles Produced during Coal Combustion. In *19th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1982; pp 1441-1449.
22. Neville, M.; Quann, R.J.; Haynes, B.S.; Sarofim, A.F. Vaporization and Condensation of Mineral Matter during Pulverized Coal Combustion. In *18th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1981; pp 1267-1274.
23. Senior, C.L.; Flagan, R.C. Ash Vaporization and Condensation during Combustion of a Suspended Coal Particle; *Aerosol Sci. Technol.* **1982**, *1*, 371-383.
24. Peshty, A.J.; Flagan, R.C.; Seinfeld, J.H. The Effect of a Growing Aerosol on the Rate of Homogeneous Nucleation of a Vapor; *J. Colloid Interface Sci.* **1981**, *82(2)*, 465-479.
25. Amdur, M.O.; Sarofim, A.F.; Neville, M.; Quann, R.J.; McCarthy, J.F.; Elliot, J.F.; Lam, H.F.; Rogers, A.E.; Conner, M.W. Coal Combustion Aerosols and SO_2: An Interdisciplinary Approach; *Environ. Sci. Technol.* **1986**, *20(2)*, 138-145.
26. Amdur, M. Animal Toxicology. In *Particles In Our Air: Concentrations and Health Effects;* Wilson, R., Spengler, J., Eds.; Harvard University Press: Cambridge, MA, 1996; pp 85-122.
27. Kittelson, D.B. Engines and Nanoparticles: A Review; *J. Aerosol Sci.* **1998**, *29(5/6)*, 575-588.
28. Dobbins, R.A.; Subramaniasivam, H. Soot Precursor Particles in Flames. In *Soot Formation in Combustion;* Bockhorn, H., Ed.; Springer Series in Chemical Physics; Springer-Verlag: Berlin, 1994; pp 290-301.
29. Howard, J.B.; Wersborg, B.L.; Williams, G.C. Coagulation of Carbon Particles in Premixed Flames; *Faraday Symp. Chem. Soc.* **1973**, *7*, 109-119.
30. Bockhorn, H. *Soot Formation in Combustion, Mechanisms and Models*; Springer Series in Chemical Physics; Springer-Verlag: Berlin, 1994; Vol. 59.
31. Palmer, H.B.; Cullis, C.F. *Chem. Phys. Carbon* **1965**, *1*, 265-325.
32. Haynes, B.S.; Wagner, H.G. Sooting Structure in a Laminar Diffusion Flame; *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84(5)*, 499-506.
33. Haynes, B.S. Soot and Hydrocarbons in Combustion. In *Fossil Fuel Combustion;* Sarofim, A.F., Bartok, W., Eds.; Wiley Interscience: New York, 1991; pp 261-326.
34. Kennedy, I.M. Models of Soot Formation and Oxidation; *Prog. Energy Combust. Sci.* **1997**, *23*, 95-132.
35. Gulder, O.L. Soot Particulate Formation in Combustion; *Trans. Can. Soc. Mech. Eng.* **1999**, *23*, 225-240.
36. Olsen, D.B.; Pickens, J.C. *Combust. Flame* **1984**, *57*, 199-208.
37. Appel, J.; Bockhorn, H.; Frenklach, M. Kinetic Modeling of Soot Formation with Detailed Chemistry and Physics: Laminar Premixed Flames of C2 Hydrocarbons; *Combust. Flame* **2000**, *121*, 122-136.
38. Violi, A.; D'Anna, A. Modeling of Aromatics Formation in Rich Premixed Flames. In *21st Event of the Italian Section of the Combustion Institute;* The Combustion Institute: Naples, Italy, 1998; pp 249-260.
39. Howard, J.B. On the Mechanism of Carbon Formation in Flames. In *12th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1969; pp 877-887.
40. Friedlander, S.K. *Smoke, Dust, and Haze, Fundamentals of Aerosol Behavior*; John Wiley & Sons: New York, 1976.
41. *The Mechanics of Aerosols*; Fuchs, N.A., Ed.; Translated from the Russian by R. E. Daisley and M. Fuchs, Translation edited by C. N. Davies; Macmillian: New York, 1964.
42. Gelbard, F.; Steinfeld, J. Simulation of Multicomponent Aerosol Dynamics; *J. Colloid Interface Sci.* **1978**, *78(2)*, 485-501.
43. Wu, J.J.; Flagan, R.C. A Discrete-Sectional Solution to the Aerosol Dynamic Equation; *J. Colloid Interface Sci.* **1988**, *123(2)*, 339-352.
44. Wu, C.-Y.; Biswas, P. Study of Numerical Diffusion in a Discrete-Sectional Model and Its Application to Aerosol Dynamics Simulation; *Aerosol Sci. Technol.* **1998**, *29*, 359-378.
45. Park, S.H.; Lee, K.W.; Otto, E.; Fissan, H. The Log-Normal Size Distribution Theory of Brownian Aerosol Coagulation for the Entire Particle Size Range: Part I—Analytical Solution Using the Harmonic Mean Coagulation Kernel; *J. Aerosol Sci.* **1999**, *30(1)*, 3-16.
46. Otto, E.; Fissan, H.; Park, S.H.; Lee, K.W. The Log-Normal Size Distribution Theory of Brownian Aerosol Coagulation for the Entire Particle Size Range: Part II—Analytical Solution Using Dahneke's Coagulation Kernel; *J. Aerosol Sci.* **1999**, *30(1)*, 17-34.
47. Landgrebe, J.D.; Pratsinis, S.E. Discrete-Sectional Model for Particulate Production by Gas-Phase Chemical Reaction and Aerosol Coagulation in the Free-Molecular Regime; *J. Colloid Interface Sci.* **1990**, *139(1)*, 63-86.
48. Mick, H.J.; Hospital, A.; Roth, P. Computer Simulation of Soot Particle Coagulation in Low Pressure Flames; *J. Aerosol Sci.* **1991**, *22(7)*, 831-841.
49. Jokiniemi, J.K.; Lazaridis, M.; Lehtinen, K.E.J.; Kauppinen, E.I. Numerical Simulation of Vapour-Aerosol Dynamics in Combustion Processes; *J. Aerosol Sci.* **1994**, *25(3)*, 429-446.
50. Pilinis, C.; Capaldo, K.P.; Nenes, A.; Pandis, S.N. MADM–A New Multicomponent Aerosol Dynamics Model; *Aerosol Sci. Technol.* **2000**, *32(5)*, 482-502.
51. Hinds, W.C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*; John Wiley & Sons: New York, 1982.
52. Marlow, W.H. Derivation of Aerosol Collision Rates for Singular Attractive Contact Potentials; *J. Chem. Phys.* **1980**, *73*, 6284-6287.
53. Lai, F.S.; Friedlander, S.K.; Pich, J.; Hindy, G.M. *J. Colloid Interface Sci.* **1972**, *39*, 395-405.
54. Desrosiers, R.E.; Riehl, J.W.; Ulrich, G.D.; Chiu, A.S. Submicron Fly-Ash Formation in Coal-Fired Boilers. In *17th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1978; pp 1395-1403.
55. Taylor, D.D.; Flagan, R.C. The Influence of Combustor Operation on Fine Particles from Coal Combustion; *Aerosol Sci. Technol.* **1982**, *1*, 103-117.
56. *Soot in Combustion Systems and Its Toxic Properties*; Lahaye, J., Prado, G., Eds.; NATO Conference Series, VI Materials Science v. 7; Plenum Press: New York, 1983.
57. Harris, S.J.; Weiner, A.M. *Combust. Sci. Technol.* **1984**, *38*, 75-87.
58. Sethi, V.; Biswas, P. Modeling of Particle Formation and Dynamics in a Flame Incinerator; *J. Air & Waste Manage. Assoc.* **1990**, *40(1)*, 42-46.
59. Linak, W.P.; Wendt, J.O.L. Toxic Metal Emissions from Incineration: Mechanisms and Control; *Prog. Energy Combust. Sci.* **1993**, *19*, 145-185.
60. Flagan, R.C.; Taylor, D.D. Laboratory Studies of Submicron Particles from Coal Combustion. In *18th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1981; pp 1227-1237.
61. Quann, R.J.; Sarofim, A.F. Vaporization of Refractory Oxides during Pulverized Coal Combustion. In *19th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1982; pp 1429-1440.
62. Mims, C.A.; Neville, M.; Quann, R.J.; House, K.; Sarofim, A.F. Laboratory Studies of Mineral Matter Vaporization during Coal Combustion. In *Emission Control from Stationary Power Sources: Technical, Economic, and Environmental Assessments;* Engle, A.J., Slater, S.M., Gentry, J.W., Eds.; American Institute of Chemical Engineers: New York, 1980; pp 188-194.
63. McElroy, M.W.; Carr, R.C.; Ensor, D.S.; Markowski, G.R. Size Distribution of Fine Particles from Coal Combustion; *Science* **1982**, *215*, 13-19.
64. McElroy, M.W.; Carr, R.C. Relationship between NO_x and Fine Particle Emissions. In *Joint Symposium on Stationary Combustion NO_x Control;* Electric Power Research Institute: Palo Alto, CA, 1981; pp 311-329.
65. Lindner, E.R.; Wall, T.F. Sodium-Ash Reactions during the Combustion of Pulverized Coal. In *23rd Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1991; pp 1313-1321.
66. Damle, A.S.; Ensor, D.S.; Ranade, M.B. Coal Combustion Aerosol Formation Mechanisms: A Review; *Aerosol Sci. Technol.* **1982**, *1*, 119-133.
67. Neville, M.; Sarofim, A.F. The Fate of Sodium during Pulverized Coal Combustion; *Fuel* **1985**, *64*, 384-490.
68. Seames, W.S.; Wendt, J.O.L. Partitioning of Arsenic, Selenium, and Cadmium during the Combustion of Pittsburgh and Illinois #6 Coals in a Self-Sustained Combustor; *Fuel Process. Technol.* **2000**, *63*, 179-196.
69. Haynes, B.S.; Neville, M.; Quann, R.J.; Sarofim, A.F. Factors Governing the Surface Enrichment of Fly Ash in Volatile Trace Species; *J. Colloid Interface Sci.* **1982**, *87(1)*, 266-278.
70. Davison, R.L.; Natusch, D.F.S.; Wallace, J.R.; Evans, C.A.J. Trace Elements in Fly Ash Dependence of Concentration on Particle Size; *Environ. Sci. Technol.* **1974**, *8(13)*, 1107-1113.
71. Ondov, J.M.; Ragini, R.C.; Biermann, A.H. Elemental Particle-Size Emissions from Coal-Fired Power Plants: Use of an Inertial Cascade Impactor; *Atmos. Environ.* **1978**, *12*, 1175-1185.
72. Biermann, A.H.; Ondov, J.M. Application of Surface-Deposition Models to Size-Fractionated Coal Fly Ash; *Atmos. Environ.* **1980**, *14*, 289-295.
73. Linak, W.P.; Wendt, J.O.L. Trace Metal Transformation Mechanisms during Coal Combustion; *Fuel Process. Technol.* **1994**, *39(1)*, 173-198.
74. Ondov, J.M.; Ragaini, R.C.; Biermann, A.H. Elemental Emissions from a Coal-Fired Power Plant. Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator; *Environ. Sci. Technol.* **1979**, *13(5)*, 598-607.
75. Coles, D.G.; Ragaini, R.C.; Ondov, J.M. Behaviour of Radionuclides in Western Coal-Fired Power Plants; *Environ. Sci. Technol.* **1978**, *12(4)*, 442-446.
76. Gladney, E.S.; Small, J.A.; Gordon, G.E.; Zoller, W.H. Composition and Size Distribution of In-Stack Particulate Material at a Coal-Fired Power Plant; *Atmos. Environ.* **1976**, *10*, 1071-1077.
77. Kaakinen, J.W.; Jorden, R.M.; Lawasani, M.H.; West, R.E. Trace Element Behavior in a Coal-Fired Power Plant; *Environ. Sci. Technol.* **1975**, *9(9)*, 862-869.

78. Shendrikar, A.D.; Ensor, D.S.; Cowen, S.J.; Woffinden, G.J.; McElroy, M.W. Size-Dependent Penetration of Trace Elements through a Utility Baghouse; *Atmos. Environ.* **1983**, *17(8)*, 1411-1421.
79. Klein, D.H.; Andren, A.W.; Carter, J.A.; Emery, J.F.; Feldman, C.; Fulkerson, W.; Lyon, W.S.; Ogle, J.C.; Talmi, Y.; van Hook, R.I.; Bolton, N. Pathways of Thirty-Seven Trace Elements through Coal-Fired Power Plant; *Environ. Sci. Technol.* **1975**, *9(10)*, 973-979.
80. Linak, W.P.; Peterson, T.W. Mechanisms Governing the Composition and Size Distribution of Ash Aerosol in a Laboratory Pulverized Coal Combustor. In *21st Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1986; pp 399-410.
81. Markowski, G.R.; Ensor, D.S.; Hooper, R.G.; Carr, R.C. A Submicron Aerosol Mode in Flue Gas from a Pulverized Coal Utility Boiler; *Environ. Sci. Technol.* **1980**, *14(11)*, 1400-1402.
82. Neville, M.; McCarthy, J.F.; Sarofim, A.F. Size Fractionation of Submicrometer Coal Combustion Aerosol for Chemical Analysis; *Atmos. Environ.* **1983**, *17(12)*, 2599-2604.
83. Smith, R.D.; Campbell, J.A.; Nielson, K.K. Characterization and Formation of Submicron Particles in a Coal-Fired Plant; *Atmos. Environ.* **1979**, *13*, 607.
84. Smith, R.D.; Campbell, J.A.; Nielson, K.K. Volatility of Fly Ash and Coal; *Fuel* **1980**, *59*, 661-665.
85. Senior, C.L.; Bool, L.E.I.; Morency, J.R. Laboratory Study of Trace Element Vaporization from Combustion of Pulverized Coal; *Fuel Process. Technol.* **2000**, *63*, 109-124.
86. Helble, J.J. Trace Element Behavior during Coal Combustion: Results of a Laboratory Study; *Fuel Process. Technol.* **1994**, *39(1)*, 159-172.
87. Senior, C.L.; Bool, L.E.I.; Srinivasachar, S.; Pease, B.R.; Porle, K. Pilot Scale Study of Trace Element Vaporization and Condensation during Combustion of a Pulverized Sub-Bituminous Coal; *Fuel Process. Technol.* **2000**, *63*, 149-165.
88. Linton, R.W.; Loh, A.; Natusch, D.F.S. Surface Predominance of Trace Elements in Airborne Particles; *Science* **1976**, *191*, 852-854.
89. Frandsen, F.; Dam-Johansen, K.; Rasmussen, P. Trace Elements from Combustion and Gasification of Coal—An Equilibrium Approach; *Prog. Energy Combust. Sci.* **1994**, *20(2)*, 115-138.
90. Sandelin, K.; Backman, R. A Simple Two-Reactor Method for Predicting Distribution of Trace Elements in Combustion Systems; *Environ. Sci. Technol.* **2000**, *33(24)*, 4508-4513.
91. Yousif, S.; Lockwood, F.C.; Abbas, T. Modeling of Toxic Metal Emissions from Solid Fuel Combustors. In *27th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1998; pp 1647-1654.
92. Mocellin, A.; Kingery, W.D. Microstructural Changes during Heat Treatment of Sintered Al_2O_3; *J. Amer. Ceram. Soc.* **1973**, *56(6)*, 309-314.
93. Kingery, W.D.; Bowen, H.K.; Uhlmann, D.R. *Introduction to Ceramics*; Wiley: New York, 1976.
94. Ulrich, G.D.; Subramanian, N.S. Particle Growth in Flames-3. Coalescence as a Rate-Controlling Process; *Combust. Sci. Technol.* **1984**, *17* (3-4), 119-126.
95. Pratsinis, S.E. Flame Aerosol Synthesis of Ceramic Powders; *Prog. Energy Combust. Sci.* **1998**, *24*, 197-219.
96. Woolridge, M.S. Gas-Phase Combustion Synthesis of Particles; *Prog. Energy Combust. Sci.* **1998**, *24(1)*, 63-87.
97. Muñoz, R.H.; Charalampopoulos, T.T. Evolution of Compositional and Structural Properties of Soot in Premixed Flames. In *27th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1998; pp 1471-1479.
98. Mulholland, G.W.; Liggett, W.; Koseki, H. Effect of Pool Diameter on the Properties of Smoke Produced by Crude Oil Fires. In *26th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1996; pp 1445-1452.
99. Koch, W.; Friedlander, S.K. Effect of Particle Coalescence on the Surface Area of a Coagulating Aerosol; *J. Colloid Interface Sci.* **1990**, *140*, 419-427.
100. Xiong, Y.; Pratsinis, S.E. Gas Phase Production of Particles in Reactive Turbulent Flows; *J. Aerosol Sci.* **1991**, *22(5)*, 637-655.
101. Reilly, P.T.A.; Whitten, W.B.; Ramsey, J.M. Evidence for the Emergence of Whole Mature Soot Aggregates from Single PAH-Containing Droplets. In *2000 Technical Meeting of the Central State Section of the Combustion Institute;* The Combustion Institute: Pittsburgh, PA, 2000.
102. Biswas, P.; Wu, C.Y. Control of Toxic Metal Emissions from Combustors Using Sorbents: A Review; *J. Air & Waste Manage. Assoc.* **1998**, *48(2)*, 113-127.
103. Goldstein, H.L.; Siegmund, C.W. Influence of Heavy Oil Composition and Boiler Combustion Conditions on Particulate Emission; *Environ. Sci. Technol.* **1976**, *10(12)*, 1109-1114.
104. Senior, C.L.; Zeng, T.; Che, J.; Ames, M.R.; Sarofim, A.F.; Olmez, I.; Huggins, F.E.; Shah, N.; Huffman, G.P.; Kolker, A.; Mroczkowski, S.; Palmer, C.; Finkelman, R. Distribution of Trace Elements in Selected Pulverized Coals as a Function of Particle Size and Density; *Fuel Process. Technol.* **2000**, *63(2-3)*, 215-241.
105. Huggins, F.E.; Huffman, G.P.; Lee, R.J. Scanning Electron Microscope-Based Automated Image Analysis (SEM-AIA) and Mossbauer Spectroscopy: Quantitative Characterization of Coal Minerals. In *Coal and Coal Products: Analytical Characterization Techniques;* Fuller, E.L., Ed.; American Chemical Society: 1982; pp 239-258.
106. Straszheim, W.E.; Markuzewshi, R. Characterization of Mineral Matter in Coal for Prediction of Ash Composition and Particle Size. In *Engineering Foundation Conference on Inorganic Transformations and Ash Deposition During Combustion;* ASME: 1992; pp 165-177.
107. Steadman, E.N.; Erikson, T.A.; Folkedahl, B.C.; Brekke, D.W. Coal and Ash Characterization: Digital Image Analysis Application. In *Engineering Foundation Conference on Inorganic Transformations and Ash Deposition during Combustions;* ASME: 1991; pp 147-164.
108. Yang, N.Y.C.; Baxter, L.L. Instrument and Sample Preparation Considerations for CCSEM Analysis. In *Engineering Foundation Conference on Inorganic Ash Transformations and Ash Deposition during Combustion;* ASME: 1991; pp 191-201.
109. Yu, H.; Marchek, J.E.; Adair, N.L.; Harb, J.N. Characterization of Minerals and Coal/Mineral Associations in Pulverized Coal. In *Engineering Foundation Conference on the Impact of Ash Deposition on Coal Fired Plants;* Taylor and Francis: 1993; pp 361-372.
110. Wigley, F.; Williamson, J.; Gibb, W.H. The Distribution of Mineral Matter in Pulverized Coal Particles in Relation to Burnout Behaviour; *Fuel* **1997**, *76*, 1283-1288.
111. Wilemski, G.; Srinivasachar, S.; Sarofim, A.F. Modeling of Mineral Matter Redistribution and Ash Formation in Pulverized Coal Combustion. In *Engineering Foundation Conference on Inorganic Ash Transformations and Ash Deposition during Combustion;* ASME: 1991; pp 545-564.
112. Sarofim, A.F.; Howard, J.B.; Padia, A.S. The Physical Transformation of Mineral Matter in Pulverized Coal under Simulated Combustion Conditions; *Combust. Sci. Technol.* **1977**, *16*, 187-204.
113. Kang, S.-G.; Helble, J.J.; Sarofim, A.F.; Béer, J.M. Time-Resolved Evolution of Fly Ash during Pulverized Coal Combustion. In *22nd Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1988; pp 231-238.
114. Baxter, L.L. *Coal Char Fragmentation during Pulverized Coal Combustion*; SAND95-8250 UC-1409; Sandia National Laboratories: 1995.
115. Benson, S.A.; Jones, M.L.; Harb, J.N. Ash Formation and Deposition. In *Fundamentals of Coal Combustion for Clean and Efficient Use*; Smoot, L.D., Ed.; Elsevier: New York, 1993; pp 299-373.
116. Barta, L.E.; Toqan, M.A.; Béer, J.M.; Sarofim, A.F. Prediction of Fly Ash Size and Chemical Composition Distributions: The Random Coalescence Model. In *24th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1992; pp 1135-1144.
117. Barta, L.E.; Vámos, G.; Toqan, M.A.; Béer, J.M.; Sarofim, A.F. A Statistical Investigation on Particle-to-Particle Variation of Flyash Using SEM-AIA-EDAX Technique; *Mater. Res. Soc. Symp. Proc.* **1990**, *178*, 67-81.
118. *A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP/Wet FGD System*; Batelle Columbus; DOE/PC/93251-T2; DE94017941; U.S. Department of Energy; Pittsburgh Energy Technology Center: 1994; Vol. 1.
119. Charon, O.; Sarofim, A.F.; Béer, J.M. Distribution of Mineral Matter in Pulverized Coal; *Prog. Energy Combust. Sci.* **1990**, *16*, 319-326.
120. Raask, E.; Wilkins, D.M. Volatilization of Silica in Gasification and Combustion Processes; *J. Inst. Fuel* **1965**, *38*, 255-262.
121. Kerstein, A.R.; Edwards, B.F. Percolation Model for Simulation of Char Oxidation and Fragmentation Time-Histories; *Chem. Eng. Sci.* **1987**, *42(7)*, 1629-1634.
122. Kang, S.-G. Fundamental Studies of Mineral Matter Transformation during Pulverized Coal Combustion: Residual Ash Formation. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1991.
123. Kerstein, A.R.; Niksa, S. Fragmentation during Carbon Conversion: Predictions and Measurements. In *20th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1984; pp 941-949.
124. Seggiani, M.; Bardi, A.; Vitolo, S. Prediction of Fly-Ash Size Distribution: A Correlation between Char Transition Radius and Coal Properties; *Fuel* **2000**, *79*, 999-1002.
125. Hurt, R.H.; Davis, K.A. Near-Extinction and Final Burnout in Coal Combustion. In *25th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1994; pp 561-568.
126. Wu, H.; Bryant, G.; Benfell, K.; Wall, T. Experimental Study on the Effect of System Pressure on Char Structure of an Austrialian Bituminous Coal; *Energy Fuels* **2000**, *14(2)*, 282-290.
127. Fischer, G.L.; Chang, D.P.Y.; Brummer, M. Fly Ash Collected from Electrostatic Precipitators: Micro-Crystalline Structures and the Mystery of Spheres; *Science* **1976**, *192*, 553.
128. Raask, E. *Mineral Impurities in Coal Combustion: Behavior, Problems, and Remedial Measures*; Hemisphere Publishing: New York, 1985.
129. Sloss, L.L.; Smith, I.M.; Adams, D.M.B. Pulverized Coal Ash—Requirements for Utilization; *IEA Coal Research* **1996**, *IEACR/88*.

130. McCarthy, G.J.; Solem, J.K.; Manz, O.; Hassett, D.J. Use of a Database of Chemical, Mineralogical, and Physical Properties of North American Fly Ash to Study the Nature of Fly Ash and Its Use as a Mineral Admixture in Concrete; *Miner. Res. Soc. Symp. Proc.* **1990**, *178*, 2-31.
131. Hering, S.V. *Air Sampling Instruments*; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1995.
132. D'Alessio, A.; D'Anna, A.; Gambi, G.; Minutolo, P.; Sgro, L.A.; Violi, A. Combustion-Generated Nanoparticles; *Chim. Ind.* **1999**, *81*, 1001-1006.
133. D'Alessio, A.; D'Anna, A.; Minutolo, P.; Sgro, L.A. Nanoparticles in Combustion Systems: Their Formation and Impact on Climate Change and Health Effects. In *Chemical Engineering, Greetings to Prof. Mario Dente on the Occasion of his 65th Birthday*; AIDIC, Eds.; Milano, Italy, 1999; pp 99-110.
134. Narsimhan, G.; Ruckenstein, E. The Brownian Coagulation of Aerosols over the Entire Range of Knudsen Numbers: Connection between the Sticking Probability and the Interaction Forces; *J. Colloid Interface Sci.* **1985**, *104(2)*, 344-369.
135. Graham, K.A. Submicron Ash Formation and Interaction with Sulfur Oxides During Pulverized Coal Combustion. Ph.D. Thesis, Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 1991.
136. Linak, W.P. The Effect of Coal Type, Residence Time, and Combustion Configuration on the Submicron Aerosol Composition and Size Distribution from Pulverized Coal Combustion. Ph.D. Thesis, University of Arizona, Tucson, AZ, 1985.
137. Miake-Lye, R.C.; Anderson, B.E.; Cofer, W.R.; Wallio, H.A.; Nowicki, G.D.; Ballenthin, J.O.; Hunton, D.E.; Knighton, W.B.; Miller, T.M.; Seeley, J.V.; Viggiano, A.A. SO_x Oxidation and Volatile Aerosol in Aircraft Exhaust Plumes Depend on Fuel Sulfur Content; *Geophys. Res. Lett.* **1998**, *25(10)*, 1677-1680.
138. Park, C.; Appleton, J.P. Shock-Tube Measurements of Soot Oxidation Rates; *Combust. Flame* **1973**, *20*, 369-379.
139. Itkonen, A.O.; Jantunen, M.J. Emissions and Particle-Size Distribution of Some Metallic Elements of Two Peat/Oil-Fired Boilers; *Environ. Sci. Technol.* **1986**, *20(4)*, 335.
140. *Industrial Air Pollution Control Systems*; Heumann, W.L., Ed.; McGraw Hill: New York, 1997.
141. *Handbook of Air Pollution Technology*; Calvert, S., Englund, H.M., Eds.; Wiley: New York, 1986.
142. *Air Pollution,* 3rd Ed.; Stern, A.C., Ed.; Academic Press: New York, 1976.
143. Helble, J.J. A Model for the Air Emissions of Trace Metallic Elements from Coal Combustors Equipped with Electrostatic Precipitators; *Fuel Process. Technol.* **2000**, *63*, 125-147.
144. Soud, H.N. Developments in Particulate Control for Coal Combustion; *IEA Coal Research* **1995**, *IEACR/78*.
145. Zhuang, Y.; Kim, Y.J.; Lee, T.G.; Biswas, P. Experimental and Theoretical Studies of Ultra-Fine Behavior in Electrostatic Precipitators; *J. Electrost.* **2000**, *48(3)*, 245-260.
146. Yoo, K.H.; Lee, J.S.; Oh, M.D. Charging and Collection of Submicron Particles in Two-Stage Parallel-Plate Electrostatic Precipitators; *Aerosol Sci. Technol.* **1997**, *27*, 308-323.
147. Watanabe, T.; Tochikubo, F.; Koizumi, Y.; Tsuchida, T.; Hautanen, J.; Kauppinen, E.I. Submicron Particle Agglomeration by an Electrostatic Agglomerator; *J. Electrost.* **1995**, *34*, 367-383.
148. Kauppinen, E.I.; Pakkanen, T.A. Coal Combustion Aerosols: A Field Study; *Environ. Sci. Technol.* **1990**, *24*, 1811-1818.
149. Miller, S.J.; Ness, S.R.; Weber, G.F.; Erickson, T.A.; Hassett, D.J.; Hawthorne, S.B.; Katrinak, K.A.; Louie, P.K.K. *A Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants: Phase I Results from the U.S. Department of Energy Study*; U.S. DOE Pittsburgh Energy Technology Center Contract DE-FC21-93MC30097; Energy & Environmental Research Center; University of North Dakota: 1996.
150. Chow, W.; Miller, M.J.; Torrens, I.M. Pathways of Trace Elements in Power Plants: Interim Research Results and Implications; *Fuel Process. Technol.* **1994**, *39(1)*, 5-20.
151. Moore, T. Hazardous Air Pollutants: Measuring in Micrograms; *EPRI J.* **1994**, *19(1)*, 7-15.
152. Meij, R. Trace Element Behaviour in Coal-Fired Power Plants; *Fuel Process. Technol.* **1994**, *39(1)*, 199-217.
153. *Compilation of Air Emission Factors*; AP-42; EP 4.9:42/985; U.S. Environmental Protection Agency: 1982.
154. Leaderer, B.P.; Naeher, L.; Jankun, T.; Balenger, K.; Holford, T.R.; Toth, C.; Sullivan, J.; Wolfson, J.M.; Koutrakis, P. Indoor, Outdoor and Regional Summer and Winter Concentrations of PM_{10}, $PM_{2.5}$, SO_4^{2-}, H^+, NO_3^- and NH_3 and Nitrous Acid in Homes with and without Kerosene Space Heaters; *Environ. Health Perspect.* **1999**, *107(3)*, 223-231.
155. Hildemann, L.M.; Markowski, G.R.; Jones, M.C.; Cass, G.R. Submicron Aerosol Mass Distributions of Emissions from Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat-Cooking Operations; *Aerosol Sci. Technol.* **1991**, *14*, 138-152.
156. Hildemann, L.M.; Markowski, G.R.; Cass, G.R. Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol; *Environ. Sci. Technol.* **1991**, *25(4)*, 744-759.
157. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol. 8. Boilers Burning No. 2 Distillate Fuel Oil; *Environ. Sci. Technol.* **1997**, *31(10)*, 2731-2737.
158. Watkinson, W.P.; Campen, M.J.; Costa, D.L. Cardiac Arrhythmia Induction after Exposure to Residual Oil Fly Ash Particles in a Rodent Model of Pulmonary Hypertension; *Toxicol. Sci.* **1998**, *41*, 209-216.
159. Dreher, K.L.; Jaskot, R.H.; Lehmann, J.R.; Richards, J.H.; McGee, J.K. Soluble Transition Metals Mediate Residual Oil Fly Ash-Induced Acute Lung Injury; *J. Toxicol. Environ. Health* **1997**, *50*, 285-305.
160. Samet, J.M.; Reed, W.; Ghio, A.J.; Devlin, R.B.; Carter, J.D.; Dailey, L.A.; Bromberg, P.A.; Madden, M.C. Induction of Prostaglandin H Synthase 2 in Human Airway Epithelial Cells Exposed to Residual Oil Fly Ash; *Toxicol. Appl. Pharmacol.* **1996**, *141*, 159-168.
161. Miller, C.A.; Linak, W.P.; King, C.; Wendt, J.O.L. Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler; *Combust. Sci. Technol.* **1998**, *134*, 477-502.
162. Villasenor, R.; Garcia, F. Experimental Study of the Effects of Asphaltenes on Heavy Fuel Oil Droplet Combustion; *Fuel* **1999**, *78*, 933-944.
163. Urban, D.L.; Huey, S.P.; Dryer, F.L. Evaluation of the Coke Formation Potential of Residual Fuel Oils. In *24th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1992; pp 1357-1364.
164. Linak, W.P.; Miller, C.A.; Wendt, J.O.L. Comparison of the Particle Size Distributions and Elemental Partitioning from the Combustion of Pulverized Coal and Residual Fuel Oil; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 1532-1543.
165. Galbreath, K.C.; Zygarlicke, C.J.; Huggins, F.E.; Huffman, G.P.; Wong, J.L. Chemical Speciation of Nickel in Residual Oil Fly Ash; *Energy Fuels* **1998**, *12*, 818-822.
166. Galbreath, K.C.; Zygarlicke, C.J.; D, L.T.; Huggins, F.E.; Huffman, G.P. Nickel and Chromium Speciation of Residual Oil Combustion Ash; *Combust. Sci. Technol.* **1998**, *134*, 243-262.
167. Huffman, G.P.; Huggins, F.E.; Shah, N.; Huggins, R.; Linak, W.P.; Miller, C.A.; Pumire, R.J.; Meuzelaar, H.L.C.; Seehra, M.S.; Manivannan, A. Characterization of Fine Particulate Matter Produced by Combustion of Residual Fuel Oil; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 1106-1114.
168. Smoot, L.D.; Smith, P.J. *Coal Combustion and Gasification*; Plenum Press: New York, 1985.
169. Smoot, L.D. *Fundamentals of Coal Combustion for Clean and Efficient Use*; Elsevier: New York, 1993.
170. Flagan, R.C. Submicron Particles From Coal Combustion. In *17th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1978; pp 97-104.
171. Fletcher, T.H.; Ma, J.; Rigby, J.R.; Brown, A.L.; Webb, B.W. Soot in Coal Combustion Systems; *Prog. Energy Combust. Sci.* **1997**, *23*, 283-301.
172. Sadakata, M.; Yoshino, A.; Sakai, T.; Matsuoka, H. Formation of Submicron Unburnt Carbon and NO_x from Pulverized Coal Combustion System. In *20th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1984; pp 913-920.
173. Veranth, J.M.; Pershing, D.W.; Sarofim, A.F.; Shield, J.E. Sources of Unburned Carbon in the Fly Ash Produced from Low-NO_x Pulverized Coal Combustion. In *27th Symposium (International) on Combustion, Boulder, CO*; The Combustion Institute: Pittsburgh, PA, 1998; pp 1737-1744.
174. Veranth, J.M.; Fletcher, T.H.; Pershing, D.W.; Sarofim, A.F. Measurement of Soot and Char in Pulverized Coal Fly Ash; *Fuel* **2000**, *79(9)*, 1067-1075.
175. *Characterizing Toxic Emissions from a Coal-Fired Power Plant Demonstrating the AFGD ICCT Project and a Plant Utilizing a Dry Scrubber/ Baghouse System*; Final Report Bailly Station Units 7 and 8; SRI Report SRI-ENV-94-827-7960; DOE Contract DE-AC22-93PC93254; U.S. Department of Energy, Pittsburgh Energy Technology Center; Southern Research Institute: 1994.
176. *Assessment of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP*; DOE Contract DE-AC22-93PC93252; Energy and Environmental Research Corporation; U.S. Department of Energy; Pittsburgh Energy Technology Center: 1994.
177. Lind, T.; Kauppinen, E.I.; Jokiniemi, J.K.; Maenhaut, W. A Field Study on the Trace Metal Behaviour in Atmospheric Fluidized Bed Combustion. In *25th International Symposium on Combustion;* The Combustion Institute: Pittsburgh, PA, 1994; p 201.
178. Lind, T.; Kauppinen, E.I.; Maenhaut, W.; Shah, A.; Huggins, F. Ash Vaporization in Circulating Fluidized Bed Coal Combustion; *Aerosol Sci. Technol.* **1996**, *24(3)*, 135-150.
179. Mohr, M.; Ylätalo, S.; Klippel, N.; Kauppinen, E.I.; Riccius, O.; Burtscher, H. Submicron Fly Ash Penetration through Electrostatic Precipitators at Two Coal Power Plants; *Aerosol Sci. Technol.* **1996**, *24*, 191-204.
180. Ylatalo, S.I.; Hautanen, J. Electrostatic Precipitator Penetration for Pulverized Coal Combustion; *Aerosol Sci. Technol.* **1998**, *29*, 17-30.
181. Littlejohn, R.F. Mineral Matter and Ash Distribution in "As-Fired" Samples of Pulverized Fuels; *J. Inst. Fuel* **1966**, *39*, 59-67.

182. Ulrich, G.D.; Subramanian, N.S. Particle Growth in Flames III. Coalescence as a Rate-Controlling Process; *Combust. Sci. Technol.* **1977**, *17*, 119-126.
183. Lee, C.M.; Davis, K.A.; Heap, M.P.; Eddings, E.; Sarofim, A. Modeling the Vaporization of Ash Constituents in a Coal-Fired Boiler; *Combust. Inst.*, in press.
184. Linak, W.P.; Peterson, T.W. Effect of Coal Type and Residence Time on the Submicron Aerosol Distribution from Pulverized Coal Combustion; *Aerosol Sci. Technol.* **1984**, *3*, 77-96.
185. Schmidt, E.W.; Gieseke, J.A.; Allen, J.M. Size Distribution of Fine Particulate Emissions from a Coal-Fired Power Plant; *Atmos. Environ.* **1976**, *10*, 1065-1069.
186. Couch, G.R. Power from Coal—Where to Remove Impurities? *IEA Coal Research* **1995**, *IEACR/82*.
187. Smith, K.L.; Smoot, L.D.; Fletcher, T.H.; Pugmire, R.J. *Structure and Reaction Processes of Coal;* Plenum Press: New York, 1994.
188. Zygarlicke, C.J.; Jones, M.L.; Steadman, E.N.; Benson, S.A. *Characterization of Mineral Matter in ACERC Coals*; Advanced Combustion Engineering Research Center and Environmental Systems Research Institute; University of North Dakota: 1990.
189. Itkonen, A.O.; Jantunen, M.J. The Properties of Fly Ash and Fly Ash Mutagenicity. In *Encyclopedia of Environmental Control Technology, Volume 1: Thermal Treatment of Hazardous Wastes;* Cheremisinoff, P.N., Ed.; Gulf Publishing: Houston, TX, 1989; pp 755-789.
190. Hurt, R.H.; Mitchell, R.E. Unified High-Temperature Char Combustion Kinetics for a Suite of Coals of Various Rank. In *24th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1992; pp 1243-1250.
191. Hurt, R.H.; Gibbins, J.R. Residual Carbon from Pulverized Coal-Fired Boilers: 1. Size Distribution and Combustion Reactivity; *Fuel* **1995**, *74(4)*, 471-479.
192. Freeman, E.; Gao, Y.-M.; Hurt, R.; Suuberg, E. Interactions of Carbon-Containing Fly Ash with Commercial Air-Entraining Admixtures for Concrete; *Fuel* **1997**, *76(8)*, 761-765.
193. Ratafia-Brown, J.A. Overview of Trace Element Partitioning in Flames and Furnaces of Utility Coal-Fired Boilers; *Fuel Process. Technol.* **1994**, *39(1)*, 137-154.
194. McLennan, A.R.; Bryant, G.W.; Stanmore, B.R.; Wall, T.F. Ash Formation Mechanisms during pf Combustion in Reducing Conditions; *Energy & Fuels* **2000**, *14*, 150-159.
195. Nathan, Y.; Dvorachek, M.; Pelly, I.; Mimram, U. Characterization of Coal Fly Ash from Israel; *Fuel* **1999**, *78*, 205-213.
196. Huffman, G.P.; Huggins, F.E.; Shah, N.; Shah, A. Behavior of Basic Elements during Coal Combustion; *Prog. Energy Combust. Sci.* **1990**, *16*, 243-251.
197. Nielsen, H.P.; Baxter, L.L.; Sclippab, G.; Morey, C.; Frandsen, F.J.; Dam-Johansen, K. Deposition of Potassium Salts on Heat Transfer Surfaces in Straw-Fired Boilers: A Pilot-Scale Study; *Fuel* **2000**, *79(2)*, 131-139.
198. Jenkins, B.M.; Baxter, L.L.; Miles, T.R.J.; Miles, T.R. Combustion Properties of Biomass; *Fuel Process. Technol.* **1998**, *54(1-3)*, 17-46.
199. Valmari, T.; Lind, T.; Kauppinen, E.I.; Sfiris, G.; Nilsson, K.; Maenhaut, W. Field Study on Ash Behaviour during Circulating Fluidized-Bed Combustion of Biomass. 1. Ash Formation; *Energy Fuels* **1999**, *13*, 379-389.
200. Lind, T.; Valmari, T.; Kauppinen, E.I.; Sfiris, G.; Nilsson, K.; Maenhaut, W. Volatilization of the Heavy Metals during Circulating Fluidized Bed Combustion of Forest Residue; *Environ. Sci. Technol.* **1999**, *33*, 496-502.
201. Chenevert, B.C.; Kramlich, J.C.; Nichols, K.M. Ash Characteristics of High Alkali Sawdust and Sanderdust Biomass Fuels. In *27th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1998; pp 1719-1725.
202. Robinson, A.L.; Junker, H.; Buckley, S.G.; Sclippa, G.; Baxter, L.L. Interactions between Coal and Biomass when Cofiring. In *27th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1998; pp 1351-1359.
203. Dayton, D.C.; Belle-Oudry, D.; Nordin, A. Effect of Coal Minerals on Chlorine and Alkali Metals during Biomass/Coal Cofiring; *Energy Fuels* **1999**, *13(6)*, 1203-1211.
204. Nielsen, L.B.; Jensen, L.S.; Pedersen, C.; Rokke, M.; Livbjerg, H. Field Measurements of Combustion Aerosols from Co-Firing of Coal and Straw; *J. Aerosol Sci.* **1996**, *27(Suppl 1)*, S365-S366.
205. Raunemaa, T.; Yli-Tuomi, T.; Leskinen, A.; Tissari, J.; Alander, T. Wood Combustion Aerosol and Lung Exposure Estimates; *J. Aerosol Sci.* **1999**, *30(Suppl 1)*, S735-S736.
206. Amur, G.O.; Bhattacharya, S.C. A Study of Biomass as an Energy Source in Pakistan; *RERIC International Energy J.* **1999**, *21(1)*, 25-36.
207. Albalak, R.; Keeler, G.J.; Frisancho, A.R.; Haber, M. Assesment of PM_{10} Concentrations from Domestic Biomass Fuel Combustion in Two Rural Bolivian Highland Villages; *Environ. Sci. Technol.* **1999**, *33(15)*, 2505-2509.
208. Brauer, M.; Bartlett, K.; Regaldo-Pineda, J.; Perez-Padilla, R. Assessment of Particulate Concentrations from Domestic Biomass Combustion in Rural Mexico; *Environ. Sci. Technol.* **1996**, *30(1)*, 104-109.
209. Rogge, W.F.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol. 9. Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces; *Environ. Sci. Technol.* **1998**, *32(1)*, 13-22.
210. Rau, J.A. Composition and Size Distribution of Residential Wood Smoke Particles; *Aerosol Sci. Technol.* **1989**, *10*, 181-192.
211. Purvis, C.R.; McCrillis, R.C.; Kariher, P.H. Fine Particulate Matter (PM) and Organic Speciation of Fireplace Emissions; *Environ. Sci. Technol.* **2000**, *34(9)*, 1653-1658.
212. Kozinski, J.A.; Saade, R. Effect of Biomass Burning on the Formation of Soot Particles and Heavy Hydrocarbons. An Experimental Study; *Fuel* **1998**, *77(4)*, 225-237.
213. Oanh, N.T.K.; Reutehgardh, L.B.; Dung, N.T. Emission of Polycyclic Aromatic Hydrocarbons and Particulate Matter from Domestic Combustion of Selected Fuels; *Environ. Sci. Technol.* **1999**, *33(16)*, 2703-2709.
214. Mumford, J.L.; Harris, D.B.; Wilson, W.E.; Chapman, R.S.; Cao, S.; Xian, Y.; Li, X.; Chuang, J.C.; Cooke, W.M. Lung Cancer and Indoor Air Pollution in Xuan Wei, China; *Science* **1987**, *235*, 217-220.
215. Chuang, J.C.; Cao, S.R.; Xian, Y.L.; Harris, D.B.; Mumford, J.L. Chemical Characterization of Indoor Air in Homes from Communes in Xuan Wei, China, with High Lung Cancer Mortality Rate; *Atmos. Environ.* **1992**, *26A(12)*, 2193-2201.
216. Chuang, J.C.; Wise, S.A.; Cao, S.; Mumford, J.L. Chemical Characterization of Mutagenic Fractions of Particles from Indoor Coal Combustion: A Study of Lung Cancer in Xuan Wei, China; *Environ. Sci. Technol.* **1992**, *26*, 999-1004.
217. Mumford, J.L.; Helmes, C.T.; Lee, X.; Seidenberg, J.; Nesnow, S. Mouse Skin Tumorigenicity Studies of Indoor Coal and Wood Combustion Emissions from Homes for Residents in Xuan Wei, China with High Lung Cancer Mortality; *Carcinogenesis* **1990**, *11(3)*, 397-404.
218. Christopher, S.A.; Wang, M.; Berendes, T.A.; Welch, R.M.; Yang, S.-K. 1985 Biomass Burning Season in South America: Satellite Remote Sensing of Fires, Smoke, and Regional Radiative Energy Budgets; *J. Appl. Meteorology* **1998**, *37(7)*, 661-678.
219. *Recommendations for Improving Western Vistas*; Grand Canyon Visibility Transport Commission: 1996.
220. Husar, R.B.; Schichtel, B.A.; Falke, C.R.; Wilson, W.E. Dust and Smoke Events over the USA in 1998. In *Proceedings of PM2000–Particulate Matter and Health,* Charleston, SC, 2000; Air and Waste Management Association: Pittsburgh, PA, 2000; Session 10AS, p 22-23.
221. *Areas Affected by PM10 Natural Events*. Memorandum issued by M.D. Nichols, Assistant Administrator for Air and Radiation to Regional Directors; U.S. Environmental Protection Agency, 1996.
222. Ward, D.E. Factors Influencing the Emissions of Gases and Particulate Matter from Biomass Burning. In *Fire in the Tropical Biota: Ecosystem Processes and Global Challenges;* Goldammer, J.G., Ed.; Ecological Studies; Springer Verlag: Berlin, 1990; pp 418-436.
223. Jenkins, B.M.; Jones, A.D.; Turn, S.Q.; Williams, R.B. Emission Factors for Polycyclic Aromatic Hydrocarbons from Biomass Burning; *Environ. Sci. Technol.* **1996**, *30*, 2462-2469.
224. Jenkins, B.M.; Jones, A.D.; Turn, S.Q.; Williams, R.B. Particle Concentrations, Gas-Particle Partitioning, and Species Correlations for Polycyclic Aromatic Hydrocarbons (PAH) Emitted during Biomass Burning; *Atmos. Environ.* **1996**, *30(22)*, 3825-3835.
225. Walton, W.D.; Evans, D.D.; McGrattan, K.B.; Baum, H.R.; Twilley, W.H.; Madrzykowski, D.; Putorti, A.D.; Rehm, R.G.; Koseki, H.; Tennyson, E.J. In Situ Burning of Oil Spills: Mesoscale Experiments and Analysis. In *16th Arctic and Marine Oil Spill Program Technical Seminar;* Ministry of Supply and Services: Calgary, Alberta, Canada, 1993; pp 679-734.
226. Evans, D.; Walton, W.; Baum, H.; Mulholland, G.; Lawson, J.; Koseki, H. Smoke Emission from Burning Crude Oil. In *14th Arctic and Marine Oil Spill Technical Seminar;* Ministry of Supply and Services: Vancouver, British Columbia, Canada, 1991; pp 421-449.
227. Williams, J.M.; Gritzo, L.A. In Situ Sampling and Transmission Electron Microscope Analysis of Soot in the Flame Zone of Large Pool Fires. In *27th Symposium (International) on Combustion;* The Combustion Institute: Pittsburgh, PA, 1998; pp 2707-2714.
228. Dobbins, R.A.; Megaridis, C.M. Morphology of Flame-Generated Soot as Determined by Thermophoretic Sampling; *Langmuir* **1987**, *3*, 254-259.
229. Benner, B.A.J.; Bryner, N.P.; Wise, S.A.; Mulholland, G.W.; Lao, R.C.; Fingas, M.F. Polycyclic Aromatic Hydrocarbon Emissions from the Combustion of Crude Oil on Water; *Environ. Sci. Technol.* **1990**, *24*, 1418-1427.
230. Barton, R.G.; Clark, W.D.; Seeker, W.R. Fate of Metals in Waste Combustion Systems; *Combust. Sci. Technol.* **1990**, *74*, 327-342.
231. Lighty, J.S.; Veranth, J.M. The Role of Research in Practical Incineration Systems—A Look at the Past and the Future. In *27th Symposium (International) on Combustion, Boulder, CO*; The Combustion Institute: Pittsburgh, PA, 1998; pp 1255-1273.
232. Durlak, S.K.; Biswas, P.; Shi, J. Equilibrium Analysis of the Effect of Temperature, Moisture and Sodium Content on Heavy Metal Emissions from Municipal Solid Waste Incinerators; *J. Hazard. Mater.* **1997**, *56*, 1-20.

233. Holbert, C.; Lighty, J.S. Trace Metals Behavior during Thermal Treatment of Sludge Wastes; *J. Waste Manage.* **1999**, *18*, 423-431.
234. Smith, J.D.; Vandell, R.; Hixon, E.M. Application of Computational Fluid Mechanics to Modeling the Incineration of Chlorinated Hydrocarbon Wastes in Thermal Oxidizers; *Combust. Sci. Technol.* **1994**, *101*, 397-423.
235. Lee, C.C. A Model Analysis of Metal Partitioning in a Hazardous Waste Incineration System; *J. Air Pollut. Control Assoc.* **1988**, *38(7)*, 941-945.
236. Wey, M.-Y.; Hwang, J.-H.; Chen, J.-C. Mass and Elemental Size Distribution of Chromium, Lead, and Cadmium under Various Incineration Conditions; *J. Chem. Eng. Jpn.* **1998**, *31(4)*, 506-517.
237. Eddings, E.G.; Lighty, J.S.; Kozinski, J.A. Determination of Metal Behavior during the Incineration of a Contaminated Montmorillonite Clay; *Environ. Sci. Technol.* **1994**, *28*, 1791-1800.
238. Rink, K.K.; Kozinski, J.A.; Lighty, J.S. Biosludge Incineration in FBCs: Behavior of Ash Particles; *Combust. Flame* **1995**, *100*, 121-130.
239. Biswas, P.; Zachariah, M.R. In Situ Immobilization of Lead Species in Combustion Environments by Injection of Gas Phase Silical Sorbent Precursors; *Environ. Sci. Technol.* **1997**, *31(9)*, 2455-2463.
240. Wendt, J.O.L. Mechanisms Governing the Partitioning of Semi-Volatile Alkali and Toxic Metals during Waste and Waste Fuel Combustion. In *1st International Symposium on Incineration and Flue Gas Treatment Technologies;* Sheffield University, United Kingdom: 1997.
241. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Metal Aerosol Formation in a Laboratory Swirl Flame Incinerator. In *3rd International Congress on Toxic Combustion Byproducts;* Cambridge, MA: 1993.
242. Linak, W.P.; Ryan, J.V.; Wendt, J.O.L. Formation and Destruction of Hexavalent Chromium in a Laboratory Swirl Flame Incinerator; *Combust. Sci. Technol.* **1996**, *116-117(1-6)*, 479-498.
243. Chen, J.-C.; Wey, M.-Y. Simulation of Hexavalent Chromium Formation under Various Incineration Conditions; *Chemosphere* **1998**, *36(7)*, 1553-1564.
244. *Draft Test Report: A Performance Test on a Spray Dryer, Fabric Filter, Wet Scrubber System*; Radian Corporation; Report prepared for Shiva Garg; Office of Solid Waste; U.S. Environmental Protection Agency: 1989.
245. Kauppinen, E.I.; Pakkanen, T.A. Mass and Trace Element Size Distributions of Aerosols Emitted by a Hospital Refuse Incinerator; *Atmos. Environ.* **1990**, *24A*, 423-429.
246. Heywood, J.B. Future Engine Technology. Lessons from the 1980s for the 1990s; *J. Eng. Gas Turbines & Power, Transactions of the ASME* **1991**, *113(3)*, 319-330.
247. Khair, M.K. Progress in Diesel Engine Emissions Control; *J. Eng. Gas Turbines & Power, Transactions of the ASME* **1992**, *114(3)*, 568-577.
248. Degobert, P. *Automobiles and Pollution*; Society of Automotive Engineers: Warrendale, PA, 1995.
249. *Diesel Engines: Combustion and Emissions*; Society of Automotive Engineers: Warrendale, PA, 1999; Vol. SP-1484.
250. *Diesel Combustion, Emissions, and Exhaust Aftertreatment*; EI93010685312; Society of Automotive Engineers: Warrendale, PA, 1992.
251. Johnson, J.H.; Baines, T.M.; Clerc, J.C. *Diesel Particulate Emissions: Measurement Techniques, Fuel Effects and Control Technology*; Society of Automotive Engineers: Warrendale, PA, 1992; Vol. PT-42.
252. *Processes of Diesel Engine Combustion SP-1444*; Society of Automotive Engineers: Warrendale, PA, 1999.
253. Zhao, H.; Ladommatos, N. Optical Diagnostics for Soot and Temperature Measurements in Diesel Engines; *Prog. Energy Combust. Sci.* **1998**, *24(3)*, 221-255.
254. van Beckhoven, L.C. *Effects of Fuel Properties on Diesel Engine Emissions. A Review of Information Available to the EEC-MVEG Group*; SAE Technical Paper Series; Society of Automotive Engineers: Warrendale, PA, 1991.
255. Koltsakis, G.C.; Stametelos, A.M. Catalytic Automotive Exhaust Aftertreatment; *Prog. Energy Combust. Sci.* **1997**, *23(1)*, 1-39.
256. Neeft, J.P.A.; Makkee, M.; Moulijn, J.A. Diesel Particulate Emission Control; *Fuel Process. Technol.* **1996**, *47(1)*, 1-69.
257. Heywood, J.B. *Internal Combustion Engine Fundamentals*; McGraw Hill: New York, 1988.
258. *Handbook of Air Pollution from Internal Combustion Engines Pollutant Formation and Control*; Sher, E., Ed.; Academic Press: Boston, MA, 1998.
259. Flynn, P.F.; Durrett, R.; Hunter, G.; zur Loye, A.; Akinyemi, O.C.; Dec, J.; Westbrook, C. *Diesel Combustion: An Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation*; 1999-01-0509; Society of Automotive Engineers: Warrendale, PA, 1999.
260. Bagley, S.T.; Baumgard, K.J.; Gratz, L.D.; Johnson, J.H.; Leddy, D.G. *Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions*; Research Report 76; Health Effects Institute: Cambridge, MA, 1996.
261. Ristovski, Z.D.; Morawska, L.; Bofinger, N.D.; Hitchins, J. Submicrometer and Supermicrometer Particulate Emission from Spark Ignition Vehicles; *Environ. Sci. Technol.* **1998**, *32(24)*, 3845-3852.
262. Abdul-Khalek, I.S.; Kittelson, D.B.; Graskow, B.R.; Wei, Q.; Brear, F. *Diesel Exhaust Particle Size: Measurement Issues and Trends*; 980525; Society of Automotive Engineers: Warrendale, PA, 1998.
263. Morawska, L.; Bofinger, N.D.; Kocis, L.; Nwankwoala, A. Submicrometer and Supermicrometer Particles Form Diesel Vehicle Emissions; *Environ. Sci. Technol.* **1998**, *32(14)*, 2033-2042.
264. Graskow, B.R.; Kittelson, D.B.; Abdul-Khalek, I.S.; Ahmadi, M.R.; Morris, J.E. *Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine*; 980528; Society of Automotive Engineers: Warrendale, PA, 1998.
265. Maricq, M.M.; Podsiadlik, D.H.; Chase, R.E. Examination of the Size-Resolved and Transient Nature of Motor Vehicle Particle Emissions; *Environ. Sci. Technol.* **1999**, *33(10)*, 1618-1626.
266. Maricq, M.M.; Podsiadlik, D.H.; Chase, R.E. Gasoline Vehicle Particle Size Distributions: Comparison of Steady State, FTP, and US06 Measurements; *Environ. Sci. Technol.* **1999**, *33(12)*, 2007-2015.
267. Harrison, R.M.; Jones, M.; Collins, G. Measurements of the Physical Properties of Particles in the Urban Atmosphere; *Atmos. Environ.* **1999**, *33*, 309-321.
268. Hitchins, J.; Morawska, L.; Wolff, R.; Gilbert, D. Concentrations of Submicrometre Particles from Vehicle Emissions near a Major Road; *Atmos. Environ.* **1999**, *34*, 51-59.
269. Kittelson, D.B.; Dolan, D.F.; Oliver, R.B.; Aufderheide, E. Diesel Exhaust Particle Size Distributions–Fuel and Additive Effects. In *The Measurement and Control of Diesel Particulate Emissions;* Progress in Techology Series No. 17; Society of Automotive Engineers: Warrendale, PA, 1979; pp 233-244.
270. Kalghatgi, G.T. *Deposits in Gasoline Engines–A Literature Review*; SAE Paper 902108; Society of Automotive Engineers: Warrendale, PA, 1990.
271. Kayes, D.; Hochgreb, S. Mechanisms of Particulate Matter Formation in Spark-Ignition Engines. 2. Effect of Fuel, Oil, and Catalyst Parameters; *Environ. Sci. Technol.* **1999**, *33*, 3968-3977.
272. Sagebiel, J.C.; Zielinska, B.; Walsh, P.A.; Chow, J.C.; Cadle, S.H.; Mulawa, P.A.; Knapp, K.T.; Zweidinger, R.B.; Snow, R. PM10 Exhaust Samples Collected during IM-240 Dynamometer Tests of In-Service Vehicles in Nevada; *Environ. Sci. Technol.* **1997**, *31(1)*, 75-83.
273. Hawley, J.G.; Brace, C.J.; Wallace, F.J.; Horrocks, R.W. Combustion-Related Emissions in CI Engines. In *Handbook of Air Pollution from Internal Combustion Engines;* Sher, E., Ed.; Academic Press: Boston, MA, 1998; pp 280-357.
274. Tanaka, S.; Shimizu, T. A Study of Composition and Size Distribution of Particulate Matter from DI Diesel Engine SAE 1999-01-3487. In *Diesel Engines: Combustion and Emissions;* Society of Automotive Engineers: Warrendale, PA, 1999.
275. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R. Sources of Fine Organic Aerosol 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks; *Environ. Sci. Technol.* **1993**, *27(4)*, 636-651.
276. Schauer, J.J.; Kleenam, M.J.; Cass, G.R.; Simoneit, B.R.T. Measurement of Emission from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks; *Environ. Sci. Technol.* **1999**, *33(10)*, 1578-1587.
277. *Emission Regulations for New Otto-Cycle and Diesel-Cycle Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures;* 40CFR86 Subpart N; Office of the Federal Registrar; U.S. Government Printing Office: 1998.
278. Hildemann, L.M.; Cass, G.R.; Markowski, G.R. A Dilution Stack Sampler for Collection of Organic Aerosol Emissions: Design, Characterization, and Field Tests; *Aerosol Sci. Technol.* **1989**, *10*, 193-204.
279. Ball, J.C. *Emission Rates and Elemental Composition of Particles Collected from 1995 Ford Vehicles Using the Urban Dynamometer Driving Schedule, The Highway Fuel Economy Test, and the US06 Driving Cycle*; SAE 972914; Society of Automotive Engineers: Warrendale, PA, 1997.
280. Cadle, S.H.; Mulawa, P.A.; Ball, J.; Donase, C.; Weibel, A.; Sagebiel, J.C.; Knapp, K.T.; Snow, R. Particulate Emission Rates from In-Use High-Emitting Vehicles Recruited in Orange County, California; *Environ. Sci. Technol.* **1997**, *31(12)*, 3405-3412.
281. Williams, D.J. Particulate Emissions from "In-Use" Motor Vehicles. 1. Spark Ignition Engines; *Atmos. Environ.* **1989**, *23*, 2639-2645.
282. Zayed, J.; Hong, B.; L'Espérance, G. Characterization of Manganese-Containing Particles Collected from the Exhaust Emissions of Automobiles Running with MMT Additive; *Environ. Sci. Technol.* **1999**, *33(19)*, 3341-3346.
283. Rote, D.M. *Impact of Aircraft Emissions on Air Quality in the Vicinity of Airports, Volume III: Air Quality and Emission Modeling Needs*; FAA Report FAA-EE-84-13; USAF Report ESL-TR-84-35; U.S. Department of Transportation Federal Aviation Administration: 1984.
284. Douglas, E. *Effectiveness of Fuel Additives in Reducing Visible Emissions from J79-GE-15A Gas Turbine Engines*; ASEO Report No. 3-96; Aircraft Environmental Support Office; Naval Aviation Depot: 1996.
285. Petzold, A.; Schröder, F.P. Jet Engine Exhaust Aerosol Characterization; *Aerosol Sci. Technol.* **1998**, *28*, 62-76.
286. Anderson, B.E.; Cofer, W.R.; Bagwell, D.R.; Barrick, J.W.; Hudgins, C.H.; Burke, K.E. Airborne Observations of Aircraft Aerosol Emissions I: Total Nonvolatile Particle Emission Indices; *Geophys. Res. Lett.* **1998**, *25(10)*, 1689-1692.
287. Hagen, D.; Whitefield, P.; Paladino, J.; Trueblood, M.; Lilenfeld, H. Particle Sizing and Emission Indices for a Jet Engine Exhaust Sampled at Cruise Altitude; *Geophys. Res. Lett.* **1998**, *25(10)*, 1681-1684.

288. Hagen, D.E.; Trueblood, M.B.; Whitefield, P.D. A Field Sampling of Jet Exhaust Aerosols; *Part. Sci. Technol.* **1992**, *10*, 53-63.
289. Jones, R.E. Gas Turbine Emissions—Problems, Progress, and Future; *Prog. Energy Combust. Sci.* **1978**, *4*, 73-112.
290. Stockham, J.D.; Luebcke, E.H.; Fenton, D.L.; Johnson, R.H.; Campbell, P.P. *Turbine Engine Particulate Emission Characterization*; FAA-RD-79-15; Federal Aviation Administration: 1979.
291. Wilson, W.E.; Mage, D.T.; Grant, L.D. Estimating Separately Personal Exposure to Ambient and Non-Ambient Particulate Matter for Epidemiology and Risk Assessment: Why and How, *J. Air & Waste Manage. Assoc.* **2000**, *50*, 1167-1183.
292. Lillquist, D.R.; Lee, J.S.; Ramsey, J.R.; Boucher, K.M.; Walton, Z.L.; Lyon, J.L. A Comparison of Indoor/Outdoor PM_{10} Concentrations Measured at Three Hospitals and a Centrally Located Monitor in Utah; *Appl. Occup. Environ. Hyg.* **1998**, *13(6)*, 409-415.
293. Whitby, K.T.; Sverdrup, G.M. California Aerosols: Their Physical and Chemical Characteristics. In *The Character and Origins of Atmospheric Aerosols: A Digest of Results from the California Aerosol Characterization Experiment (ACHEX);* Hidy, G.M., et al., Eds.; Advances in Environmental Science and Technology; Wiley: New York, 1980; pp 477-517.
294. Watson, J.G.; Chow, J.C. *Reconciling Urban Fugitive Dust Emissions Inventory and Ambient Source Concentration Estimates: Summary of Current Knowledge and Needed Research*; DRI Document No. 6110.4D2; Desert Research Institute: 1999.
295. Harrison, R.M.; Brimblecombe, P.; Derwent, R.G.; Dollard, G.J.; Eggleston, S.; Hamilton, R.S.; Hickman, A.J.; Holman, C.; Laxen, D.P.H.; Moorcroft, S. *Airborne Particulate Matter in the United Kingdom*; Third Report of the Quality of Urban Air Review Group; Department of the Environment; University of Birmingham, United Kingdom: 1996.
296. Ahuja, K.O.; Paskind, J.J.; Houck, J.E.; Chow, J.C. Design of a Study for the Chemical and Size Characterization of Particulate Matter Emissions from Selected Sources in California. In *Transactions, Receptor Models in Air Resources Management;* Watson, J.G., Ed.; Air & Waste Management Association: Pittsburgh, PA, 1989; pp 145-158.
297. Jaenicke, R. Tropospheric Aerosols. In *Aerosol-Cloud-Climate Interactions;* Hobbs, P.V., Ed.; Academic Press: San Diego, CA, 1993; pp 1-31.
298. Hughes, L.C.; Cass, G.R.; Gone, J.; Ames, M.; Olmez, I. Physical and Chemical Characterization of Atmospheric Ultrafine Particulates in the Los Angeles Area; *Environ. Sci. Technol.* **1998**, *32(9)*, 1153-1161.
299. Penchin, P.M. National PM Study: OPPE Particulate Programs Evaluation System, 1994. In *Particles In Our Air*; Wilson, R., Spengler, J., Eds.; Harvard University Press: 1996.
300. *National Air Quality and Emissions Trends Report, 1997*; EPA 454/R-98-016; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: 1998.
301. *Latest Findings on National Air Quality: 1997 Status and Trends*; EPA 454/F-98-009; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: 1998.
302. Chen, M.L.; Mao, I.F.; Lin, I.K. The $PM_{2.5}$ and PM_{10} Particles in Urban Areas of Taiwan; *Sci. Total Environ.* **1999**, *226(2-3)*, 227-235.
303. Chen, W.-C.; Wang, C.-S.; Wei, C.-C. Assessment of Source Contributions to Ambient Aerosols in Taiwan; *J. Air & Waste Manage. Assoc.* **1997**, *47(4)*, 501-509.
304. Tuch, T.; Brand, P.; Wichmann, H.E.; Heyder, J. Variation of Particle Number and Mass Concentration in Various Size Ranges of Ambient Aerosol in Eastern Germany; *Atmos. Environ.* **1997**, *31(24)*, 4193-4197.
305. *Air Quality Criteria for Particulate Matter*; EPA/600/P-95-001 aF thru cF; U.S. Environmental Protection Agency: 1996.
306. *Receptor Modeling for Air Quality Management*; Hopke, P.K., Ed.; Data Handling in Science and Technology; Elsevier: New York, 1991.
307. Watson, J.G.; Robinson, N.F.; Fujita, E.M.; Chow, J.C.; Pace, T.G.; Lewis, C.; Coulter, T. *CMB8–Applications and Validation Protocol for $PM_{2.5}$ and VOCS*; DRI Document No. 1980.2D1; Desert Research Institute: 1998.
308. Cass, G.R.; Gray, H.A. *Regional Emissions and Atmospheric Concentrations of Diesel Engine Particulate Matter: Los Angeles as a Case Study in Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects*; Health Effects Institute: 1995.
309. Kleeman, M.J.; Eldering, A.; Cass, G.R. Modeling the Airborne Particulate Complex as a Source-Oriented External Mixture; *J. Geophys. Res.* **1997**, *102(D17)*, 21,355-21,372.
310. Kleeman, M.J.; Cass, G.R. Source Contributions to the Size and Composition Distribution of the Urban Particulate Air Pollution; *Atmos. Environ.* **1998**, *32(16)*, 2803-2816.
311. Evelyn, J. Fumigorum or the Inconvenience of the Aer and Smoake of London Dessispated: Together with Some Remdies Hombly Proposed, 1661. Cited in *Advances in Environmental Science*; Pitts, Metcalf, Eds.; Wiley-Interscience: New York, 1969.
312. Bonfanti, L.; De Michele, G.; Riccardi, J.; Lopes-Doriga, E. Influence of Coal Type and Operating Conditions on the Formation of Incomplete Combustion Products. Pilot Plant Experiments; *Combust. Sci. Technol.* **1994**, *10*, 505-525.
313. Busch, R.H.; Buschbom, R.L.; Cannon, W.C.; Lauhala, K.E.; Miller, F.J.; Graham, J.A.; Smith, L.G. Effects of Ammonium Nitrate Aerosol Exposure on Lung Structure of Normal and Elastase-Impaired Rats and Guinea Pigs; *Environ. Res.* **1986**, *39(2)*, 237-252.
314. Carter, J.D.; Ghio, A.J.; Samet, J.M.; Devlin, R.B. Cytokine Production by Human Airway Epithelial Cells after Exposure to an Air Pollution Particle Is Metal-Dependent; *Toxicol. Appl. Pharmacol.* **1997**, *146(2)*, 180-188.
315. Chen, L.C.; Lam, H.F.; Ainsworth, D.; Guty, J.; Amdur, M.O. Functional Changes in the Lungs of Guinea Pigs Exposed to Sodium Sulfite Aerosols; *Toxicol. Appl. Pharamacol.* **1987**, *89*, 1.
316. Chin, B.Y.; Choi, M.E.; Burdick, M.D.; Strieter, R.M.; Risby, T.H.; Choi, A.M. Induction of Apoptosis by Particulate Matter: Role of TNF-Alpha and MAPK; *Am. J. Physiol.* **1998**, *275(5 Pt 1)*, L942-949.
317. Costa, D.L.; Dreher, K.L. Bioavailable Transition Metals in Particulate Matter Mediate Cardiopulmonary Injury in Healthy and Compromised Animal Models; *Environ. Health Perspect.* **1997**, *105(Suppl 5)*, 1053-1060.
318. Dockery, D.W.; Pope, A.C.; Xiping, X.; Spengler, J.D.; Ware, J.H.; Fay, M.E.; Ferris, B.G.; Speizer, F.E. An Association between Air Pollution and Mortality in Six U.S. Cities; *New Engl. J. Med.* **1993**, *329(24)*, 1753-1759.
319. Donaldson, K. Local Inflammatory and Systemic Effects Following Short-Term Inhalation Exposure to Fine and Ultrafine Carbon Black in Rats. In *The Health Effects of Fine Particles: Key Questions and the 2003 Review, Brussels, Belgium*; Health Effects Institute: Cambridge, MA, 1999; pp II-171.
320. Elder, A.C.P.; Gelein, R.; Finkelstein, J.N.; Cox, C.; Oberdörster, G. Endotoxin Priming Affects the Lung Response to Ultrafine Particles and Ozone in Young and Old Rats; *Inhal. Toxicol.* **2000**, *12(Suppl 1)*, 85-98.
321. *An Acid Aerosols Issue Paper: Health Effects and Aerometrics*; EPA-600/8-88-005F, NTIS PB91-125864; U.S. Environmental Protection Agency: 1989.
322. Frampton, M.W.; Ghio, A.J.; Samet, J.M.; Carson, J.L.; Carter, J.D.; Devlin, R.B. Effects of Aqueous Extracts of PM_{10} Filters from the Utah Valley on Human Airway Epithelial Cells; *Lung Cell. Mol. Physiol.* **1999**, *21*, L960-L967.
323. Gong, H.; Sioutas, C.; Linn, W.S.; Clark, K.W.; Terrell, S.L.; Terrell, L.L.; Anderson, K.R.; Kim, S.; Chang, M.-C. Controlled Human Exposures to Concentrated Ambient Fine Particles in Metropolitan Los Angeles: Methodology and Preliminary Health-Effect Findings; *Inhal. Toxicol.* **2000**, *12(Suppl 1)*, 107-119.
324. *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects*; Health Effects Institute: Cambridge, MA, 1995.
325. Hoek, G.; Schwartz, J.D.; Groot, B.; Eilers, P. Effects of Ambient Particulate Matter and Ozone on Daily Mortality in Rotterdam, The Netherlands; *Arch. Environ. Health* **1997**, *52(6)*, 455-463.
326. Kadiiska, M.B.; Mason, R.P.; Dreher, K.L.; Costa, D.L.; Ghio, A.J. In Vivo Evidence of Free Radical Formation in the Rat Lung after Exposure to an Emission Source Air Pollution Particle; *Chem. Res. Toxicol.* **1997**, *10(10)*, 1104-1108.
327. Kennedy, T.; Ghio, A.J.; Reed, W.; Samet, J.; Zagorski, J.; Quay, J.; Carter, J.; Dailey, L.; Hoidal, J.R.; Devlin, R.B. Copper-Dependent Inflammation and Nuclear Factor-kB Activation by Particulate Air Pollution; *Am. J. Respir. Cell Mol. Biol.* **1998**, *19*, 1-14.
328. Lewtas, J. Genotoxicity of Complex Mixtures: Strategies for the Identification and Comparative Assessment of Airborne Mutagens and Carcinogens from Combustion Sources; *Fundam. Appl. Toxicol.* **1988**, *10*, 571-589.
329. Li, X.Y.; Brown, D.; Smith, S.; MacNee, W.; Donaldson, K. Short-Term Inflammatory Responses following Intratracheal Instillation of Fine and Ultrafine Carbon Black in Rats; *Inhal. Toxicol.* **1999**, *11(8)*, 709-731.
330. Nikula, K.J.; Snipes, M.B.; Barr, E.B.; Griffith, W.C.; Henderson, R.F.; Mauderly, J.L. Comparative Pulmonary Toxicities and Carcinogenicities of Chronically Inhaled Diesel Exhaust and Carbon Black in F344 Rats; *Fundam. Appl. Toxicol.* **1995**, *25(1)*, 80-94.
331. Oberdörster, G.; Ferin, J.; Gelein, R.; Soderholm, S.C.; Finkelstein, J. Role of the Alveolar Macrophage in Lung Injury; Studies with Ultrafine Particles; *Environ. Health Perspect.* **1992**, *97*, 193-199.
332. Oberdörster, G.; Ferin, J.; Lehnert, B.E. Correlation between Particle Size, In Vivo Particle Persistence, and Lung Injury; *Environ. Health Perspect.* **1994**, *102(Suppl 5)*, 173-179.
333. Pagano, P.; Zaiacomo, T.D.; Scarcella, E.; Bruni, S.; Calamosca, M. Mutagenic Activity of Total and Particle-Sized Fractions of Urban Particulate Matter; *Environ. Sci. Technol.* **1996**, *30(12)*, 3512-3516.
334. Patterson, E.; Eatough, D.J. Indoor/Outdoor Relationships for Ambient $PM_{2.5}$ and Associated Pollutants: Epidemiological Implications in Lindon, Utah; *J. Air & Waste Manage. Assoc.* **2000**, *50(1)*, 103-110.
335. Peters, A.; Wichmann, H.E.; Tuch, T.; Heinrich, J.; Heyder, J. Respiratory Effects Are Associated with the Number of Ultrafine Particles; *Am. J. Respir. Crit. Care Med.* **1997**, *155(4)*, 1376-1383.

336. Petrovic, S.; Urch, B.; Brook, J.; Datema, J.; Purdham, J.; Liu, L.; Lukic, Z.; Zimmerman, B.; Tofler, G.; Downar, E.; Cory, P.; Tarlo, S.; Broder, I.; Dales, R.; Silverman, F. Cardiorespiratory Effects of Concentrated Ambient $PM_{2.5}$: A Pilot Study Using Controlled Human Exposures; *Inhalation Toxicol.* **2000**, *12(Suppl 1)*, 173-188.
337. Pope, C.A. Epidemiology Investigations of the Health Effects of Particulate Air Pollution: Strengths and Limitations; *Appl. Occup. Environ. Hyg.* **1998**, *13(6)*, 356-363.
338. Pope, A.C.; Hill, R.W.; Villegas, G.M. Particulate Air Pollution and Daily Mortality on Utah's Wasatch Front; *Environ. Health Perspect.* **1999**, *107(7)*, 567-573.
339. Samet, J.M.; Zerer, S.L.; Kelsall, J.E.; Xu, J. Particulate Air Pollution and Mortality: The Particle Epidemiology Evaluation Project; *Appl. Occup. Environ. Health* **1998**, *13(6)*, 364-369.
340. Schwartz, J.; Dockery, D.W. Particulate Air Pollution and Daily Mortality in Steubenville, Ohio; *Am. J. Epidemiol.* **1992**, *135(1)*, 12-19.
341. Schwartz, J.; Norris, G.; Larson, T.; Shepphard, L.; Claiborne, C.; Koenig, J. Episodes of High Coarse Particle Concentrations Are Not Associated with Increased Mortality; *Environ. Health Perspect.* **1999**, *107(5)*, 339- 342.
342. Smith, K.R.; Aust, A.E. Mobilization of Iron from Urban Particulates Leads to Generation of Reactive Oxygen Species In Vitro and Induction of Ferritin Synthesis in Human Lung Epithelial Cells; *Chem. Res. Toxicol.* **1997**, *10(7)*, 828-834.
343. Smith, K.R.; Veranth, J.M.; Lighty, J.S.; Aust, A.E. Mobilization of Iron from Coal Fly Ash Was Dependent upon Particle Size and Source of Coal; *Chem. Res. Toxicol.* **1998**, *11(12)*, 1494-1500.
344. Smith, K.R.; Veranth, J.M.; Hu, A.A.; Lighty, J.S.; Aust, A.E. Interleukin-8 Levels in Human Lung Epithelial Cells Are Increased in Response to Coal Fly Ash and Vary with Bioavailability of Iron, as a Function of Particle Size and Source of Coal; *Chem. Res. Toxicol.* **2000**, *13*, 118-125.
345. Spurny, K.R. On the Physics, Chemistry and Toxicology of Ultrafine Anthropogenic, Atmospheric Aerosols (UAAA): New Advances; *Toxicol. Lett.* **1998**, *96-97*, 253-261.
346. Takenaka, S.; Dornhöfer-Takenaka, H.; Muhle, H. Alveolar Distribution of Fly Ash and of Titanium Dioxide after Long-Term Inhalation by Wistar Rats; *J. Aerosol Sci.* **1986**, *17*, 361-364.
347. Valberg, P.A.; Watson, A.Y. Lack of Concordance between Reported Lung-Cancer Risk Levels and Occupation-Specific Diesel Exhaust Exposures; *Inhalation Toxicol.* **2000**, *12(Suppl 10)*, 199-208.
348. Veranth, J.M.; Smith, K.R.; Rohrbough, J.G.; Huggins, F.; Hu, A.A.; Lighty, J.S.; Aust, A.E. Mossbauer Spectroscopy Indicates that Iron in an Aluminosilicate Glass Phase Is the Source of the Bioavailable Iron from Coal Fly Ash; *Chem. Res. Toxicol.* **2000**, *13*, 161-164.
349. Mauderly, J.L. Toxicological and Epidemiological Evidence for Health Risks from Inhaled Engine Emissions; *Environ. Health Perspect.* **1994**, *102(Suppl 4)*, 165-171.
350. Goldsmith, C.A.; Kobzik, L. Particulate Air Pollution and Asthma: A Review of Epidemiological and Biological Studies; *Rev. Environ. Health* **1999**, *14(3)*, 121-134.
351. Phalen, R.; Bell, Y.M. *Proceedings of the 3rd Colloquium on Particulate Air Pollution and Health*; Air Pollution Health Effects Laboratory; University of California: Irvine, CA, 1999.
352. *PM2000: Particulate Matter and Health—The Scientific Basis for Regulatory Decision-Making, Charleston, SC; Extended Abstract Book;* Air & Waste Management Association: Pittsburgh, PA, 2000.
353. USC, Clean Air Act, Section 109 (b)(1), 42 USC 7401. Public Law 101-549, 1990.
354. Pope, A.C. Respiratory Disease Associated with Community Air Pollution and a Steel Mill, Utah Valley; *Am. J. Pub. Health* **1989**, *89(5)*, 623-628.
355. Dockery, D.W.; Pope, C.A.I. Outdoor Air 1: Particulates. In *Topics in Environmental Epidemiology;* Steenland, K., Savitz, D.A., Eds.; Oxford University Press: New York, 1997; pp 119-166.
356. Samet, J.M.; Jaakkola, J.J.K. The Epidemiologic Approach to Investigating Outdoor Air Pollution. In *Air Pollution and Health;* Holgate, S.T., et al., Eds.; Academic Press: San Diego, CA, 1999; pp 406-460.
357. McCullagh, P.; Nelder, J.A. *Generalized Linear Models*; Chapman and Hall: London, 1989.
358. Samet, J.; Zeger, S.; Xu, J. Particulate Air Pollution and Mortality: The Particle Epidemiology Evaluation Project; *Appl. Occup. Environ. Hyg.* **1998**, *13(6)*, 364-369.
359. *Particulate Air Pollution and Daily Mortality: Analysis of the Effects of Weather and Multiple Air Pollutants*; The Phase I.B Report of the Particle Epidemiology Evaluation Project; Health Effects Institute: Cambridge, MA, 1997.
360. Watts, W.F.J. Assessment of Occupational Exposure to Diesel Emissions. In *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects;* Group, D.W., Ed.; Health Effects Institute: Cambridge, MA, 1995; pp 107-123.
361. *TLVs Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices;* American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 2000.
362. Harrison, R.M.; Yin, J. Particulate Matter in the Atmosphere: Which Particle Properties Are Important for Its Effects on Health? *Sci. Total Environ.* **2000**, *249*, 85-101.
363. Carel, R.S. Health Aspects of Air Pollution. In *Handbook of Air Pollution from Internal Combustion Engines;* Sher, E., Ed.; Academic Press: Boston, MA, 1998; pp 42-64.
364. Guyton, A.C.; Hall, J.E. *Textbook of Medical Physiology*; Saunders: Philadelphia, PA, 1996.
365. Netter, F.H. *Respiratory System: A Compilation of Paintings Depicting Anatomy and Embryology, Physiology, Pathology, Pathophysiology, and Clinical Features and Treatment of Diseases*; Divertie, M.B., Ed.; CIBA Pharmaceutical Products: Summit, NJ, 1980.
366. International Commission on Radiological Protection Task Force on Lung Dynamics; *Health Physics* **1966**, *12*, 173-207.
367. Wilson, R.; Spengler, J. *Particles in Our Air: Concentrations and Health Effects*; Harvard University Press: Cambridge, MA, 1996.
368. Lennon, S.; Zhang, Z.; Lessmann, R.; Webster, S. Experiments on Particle Deposition in the Human Upper Respiratory System; *Aerosol Sci. Technol.* **1998**, *28(5)*, 464-474.
369. Matthews, L.R. *Cardiopulmonary Anatomy and Physiology;* Lippincott: Philadelphia, PA, 1996.
370. Sioutas, C.; Koutrakis, P.; Burton, R.M. A High-Volume Small Cutpoint Virtual Impactor for Separation of Atmospheric Particulate from Gaseous Pollutants; *Part. Sci. Technol.* **1994**, *12*, 207-221.
371. Sioutas, C.; Koutrakis, P.; Burton, R.M. A Technique to Expose Animals to Concentrated Fine Ambient Aerosols; *Environ. Health Perspect.* **1995**, *103(2)*, 172-177.
372. Sioutas, C.; Koutrakis, P. Inertial Separation of Ultrafine Particles Using a Condensational Growth/Virtual Impaction System; *Aerosol Sci. Technol.* **1996**, *25*, 424-436.
373. Gordon, T.; Gerber, H.; Fang, C.P.; Chen, L.C. A Centrifugal Particle Concentrator for Use in Inhalation Toxicology; *Inhalation Toxicol.* **1999**, *11(1)*, 71-87.
374. Clarke, R.W.; Catalano, P.; Coull, B.; Koutrakis, P.; Murthy, G.G.K.; Rice, T.; Godleski, J.J. Age-Related Responses in Rats to Concentrated Urban Air Particles (CAPs); *Inhalation Toxicol.* **2000**, *12(Suppl 10)*, 73-84.
375. Godleski, J.; Verrier, R.L.; Koutrakis, P.; Catalano, P. *Mechanisms of Morbidity and Mortality from Exposure to Ambient Air Particles*; Research Report 91; Health Effects Institute: Cambridge, MA, 2000.
376. Amdur, M.O.; Chen, L.C. Furnace-Generated Acid Aerosols: Speciation and Pulmonary Effects; *Environ. Health Perspect.* **1989**, *79*, 147-150.
377. Oberdörster, G.; Gelein, R.M.; Ferin, J.; Weiss, B. Association of Particulate Air Pollution and Acute Mortality: Involvement of Ultrafine Particles? *Inhalation Toxicol.* **1995**, *7*, 111-124.
378. Fonda, M.; Petach, M.; Rogers, C.F.; Huntington, J.; Stratton, D.; Nishioka, K.; Tipo, M. Resuspension of Particles by Aerodynamic Deagglomeration; *Aerosol Sci. Technol.* **1999**, *30(6)*, 509-529.
379. Chow, J.C.; Watson, J.G.; Houck, J.E.; Pritchett, L.C.; Rogers, C.F.; Frazier, C.A.; Egami, R.T.; Ball, B.M. A Laboratory Resuspension Chamber to Measure Fugitive Dust Size Distributions and Chemical Compositions; *Atmos. Environ.* **1994**, *28(21)*, 3463-3481.
380. Kousaka, Y.; Horiuchi, T.; Endo, Y.; Aotani, S. Generation of Aerosol Particles by Boiling Suspensions; *Aerosol Sci. Technol.* **1994**, *21*, 236-240.
381. Terashima, T.; Wiggs, B.; English, D.; Hogg, J.C.; van Eeden, S.F. Phagocytosis of Small Carbon Particles (PM_{10}) by Alveolar Macrophages Stimulates the Release of Polymorphonuclear Leukocytes from Bone Marrow; *Am. J. Respir. Crit. Care Med.* **1997**, *155(4)*, 1441-1447.
382. Liu, W.K.; Wong, C.C. Cytotoxicity of Fly-Ash in Alveolar Macrophages from Hypothyroid Rats; *Toxicol. in Vitro* **1989**, *3(2)*, 95-102.
383. Kennedy, H.L. Beta Blockade, Ventricular Arrhythmias, and Sudden Cardiac Death; *Am. J. Cardiol.* **1997**, *80(9B)*, 29J-34J.
384. Dockery, D.W.; Pope, C.A.; Kanner, R.E.; Villegas, G.M.; Schwartz, J. *Daily Changes in Oxygen Saturation and Pulse Rate Associated with Particulate Air Pollution and Barometric Pressure*; Research Report 83; Health Effects Institute: Cambridge, MA, 1999; p 1-19.
385. Pope, C.A.; Verrier, R.L.; Lovett, E.G.; Larson, A.C.; Raizenne, M.E.; Kanner, R.E.; Schwartz, J.; Villegas, G.M.; Gold, D.R.; Dockery, D.W. Heart Rate Variability Associated with Particulate Air Pollution; *Am. Heart J.* **1999**, *138(5 Pt 1)*, 890-899.
386. Gold, D.R.; Litonjua, A.; Schwartz, J.; Lovett, E.; Larson, A.; Nearing, B.; Allen, G.; Verrier, M.; Cherry, R.; Verrier, R. Ambient Pollution and Heart Variability; *Circulation* **2000**, *101(11)*, 1267-1273.
387. Nelson, S.; Martin, T.R. *Cytokines in Pulmonary Disease: Infection and Inflammation*; *Lung Biology in Health and Disease*; Marcel Dekker: New York, 2000; Vol. 141.
388. Thèze, J. *The Cytokine Network and Immune Functions*; Oxford University Press: New York, 1999.
389. Seaton, A.; MacNee, W.; Donaldson, K.; Godden, D. Particulate Air Pollution and Acute Health Effects; *Lancet* **1995**, *345(8943)*, 176-178.

390. Souza, M.B.; Saldiva, P.H.; Pope, C.A.; Capelozzi, V.L. Respiratory Changes Due to Long-Term Exposure to Urban Levels of Air Pollution: A Histopathologic Study in Humans; *Chest* **1998**, *113(5)*, 1161-1162.
391. Prichard, R.J.; Ghio, A.J.; Lehmann, J.R.; Witsett, D.W.; Tepper, J.S.; Park, P.; Gilmour, M.I.; Dreher, K.L.; Costa, D.L. Oxidant Generation and Lung Injury after Particulate Air Pollutant Exposure Increase with the Concentrations of Associated Metals; *Inhal. Toxicol.* **1996**, *8(5)*, 457-477.
392. Ghio, A.J.; Stonehuerner, J.; Prichard, R.J.; Pintadosi, C.A.; Quigley, D.R.; Dreher, K.L.; Costa, D.L. Humic-Like Substances in Air Pollution Particulates Correlate with Concentrations of Transition Metals and Oxidant Generation; *Inhal. Toxicol.* **1996**, *8*, 479-494.
393. Driscoll, K.E. TNF-alpha and MIP-2: Role in Particle-Induced Inflammation and Regulation by Oxidative Stress; *Toxicol. Lett.* **2000**, *112-113*, 177-183.
394. Ghio, A.J.; Kennedy, T.P.; Whorton, A.R.; Crumbliss, A.L.; Hatch, G.E.; Hoidal, J.R. Role of Surface Complexed Iron in Oxidant Generation and Lung Inflammation Induced by Silicates, *Am. J. Physiol.* **1992**, *263*, L511-L518.
395. Lewis, R.J.J. *Sax's Dangerous Properties of Industrial Materials*; Van Nostrand Reinhold: New York, 1992; Vol. v1-v3.
396. Wallace, L.; Slonecker, T. Ambient Air Concentrations of Fine ($PM_{2.5}$) Manganese in U.S. National Parks and in California and Canadian Cities: The Possible Impact of Adding MMT to Unleaded Gasoline; *J. Air & Waste Manage. Assoc.* **1997**, *47*, 642-653.
397. Mena, I. Trace Minerals. In *Disorders of Mineral Metabolism*; Bronner, F., Coburn, J.W., Eds.; Academic Press: New York, 1981; Vol. 1.
398. Mena, I.; Horiuchi, K.; Burke, K.; Cotzias, G.C. Chronic Manganese Poisoning: Individual Susceptibility and the Absorption of Iron; *Neurology* **1969**, *19*, 1000-1006.
399. Halliwell, B.; Gutteridge, J.M.C. *Free Radicals in Biology and Medicine*; Oxford University Press: Oxford, United Kingdom, 1999.
400. Vogl, G.; Elstner, E.F. Diesel Soot Particles Catalyze the Production of Oxyradicals; *Toxicol. Lett.* **1989**, *47*, 17-23.
401. Prahalad, A.K.; Soukup, J.M.; Inmon, J.; Willis, R.; Ghio, A.J.; Becker, S.; Gallagher, J.E. Ambient Air Particles: Effects on Cellular Oxidant Radical Generation in Relation to Particulate Elemental Chemistry; *Toxicol. Appl. Pharmacol.* **1999**, *158(2)*, 81-91.
402. Veranth, J.M.; Smith, K.R.; Hu, A.A.; Lighty, J.S.; Aust, A.E. Mobilization of Iron from Coal Fly Ash Was Dependent upon the Particle Size and the Source of Coal: Analysis of Rates and Mechanisms; *Chem. Res. Toxicol.* **2000**, *13*, 382-389.
403. Veranth, J.M.; Smith, K.R.; Aust, A.E.; Dansie, S.L.; Griffith, J.B.; Hu, A.A.; Huggins, M.L.; Lighty, J.S. Coal Fly Ash and Mineral Dust for Toxicology and Particle Characterization Studies: Equipment and Methods for $PM_{2.5}$- and PM_1-Enriched Samples; *Aerosol Sci. Technol.* **2000**, *32(2)*, 127-141.
404. Fang, R.; Aust, A.E. Ferritin Induction in Human Lung Epithelial Cells as an Indicator of Intracellular Iron Mobilization from Particulates, submitted for publication.
405. Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1972.
406. Shirnamé-Moré, L. Genotoxicity of Diesel Emissions Part I: Mutagenicity and Other Genetic Effects. In *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects;* Group, D.W., Ed.; Health Effects Institute: Cambridge, MA, 1995; pp 221-242.
407. Rosenkranz, H.S. Genotoxicity of Diesel Emissions Part II: The Possible Role of Dinitropyrenes in Lung Cancer. In *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects;* Group, D.W., Ed.; Health Effects Institute: Cambridge, MA, 1995; pp 221-242.
408. Peterson, R.E.; Theobald, H.M.; Kimmel, G.L. Developmental and Reproductive Toxicity of Dioxins and Related Compounds: Cross-Species Comparisons; *Crit. Rev. Toxicol.* **1993**, *23(3)*, 285-335.
409. Kuschner, W.G.; Wong, H.; D'Alessardro, A.; Quinlan, P.; Blanc, P.D. Human Pulmonary Responses to Experimental Inhalation of High Concentration Fine and Ultrafine Magnesium Oxide Particles; *Environ. Health Perspect.* **1997**, *105(11)*, 1234-1237.
410. Baggs, R.B.; Ferin, J.; Oberdörster, G. Regression of Pulmonary Lesions Produced by Inhaled Titanium Dioxide in Rats; *Vet. Pathol.* **1997**, *34(6)*, 592-597.
411. Churg, A.; Gilks, B.; Dai, J. Induction of Fibrogenic Mediators by Fine and Ultrafine Titanium Dioxide in Rat Tracheal Explants; *Am. J. Physiol.* **1999**, *277*, L975-L982.
412. *Council Directive of 15 July 1980 on Air Quality Limit Values for Sulphur Dioxide and Suspended Particulates*; O.J. L229/30; Council of the European Communities: 1980.
413. Amdur, M.O. Sulfuric Acid: The Animals Tried to Tell Us. In the 1989 Herbert E. Stokinger Lecture; *Appl. Ind. Hyg.* **1989**, *4(8)*, 189-197.
414. EPA National Ambient Air Quality Standards for Ozone and Particulate. *Fed. Regist.* **1996**, *61(114)*, 29719-29725.
415. *Research Priorities for Airborne Particulate Matter: I. Immediate Priorities and a Long-Range Research Portfolio*; National Research Council; National Academy Press: Washington, DC, 1998.
416. *Research Priorities for Airborne Particulate Matter: II. Evaluating Research Progress and Updating the Portfolio*; National Research Council; National Academy Press: Washington, DC, 1999.
417. EPA Final Regional Haze Regulations for Protection of Visibility in National Parks and Wilderness Areas. *Fed. Regist.* **1999**, *64(126)*, 35713-35774.
418. Tang, H.; Lewis, E.A.; Eatough, D.J.; Burton, R.M.; Farber, R.J. Determination of the Particle Size Distribution and Chemical Composition of Semi-Volatile Organic Compounds in Atmospheric Fine Particles with a Diffusion Denuder Sampling System; *Atmos. Environ.* **1994**, *28(5)*, 939-947.
419. Cui, W.; Eatough, D.J.; Eatough, N.L. Fine Particulate Organic Matter in the Los Angeles Basin–I: Assessment of the High-Volume Brigham Young University Organic Sampling System BIG BOSS; *J. Air & Waste Manage. Assoc.* **1998**, *48(11)*, 1024-1037.
420. Corio, L.A.; Sherwell, J. In-Stack Condensable Particulate Matter Measurements and Issues; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 207-218.
421. Lipkea, W.H.; Johnson, J.H.; Vuk, C.T. The Physical and Chemical Character of Diesel Particulate Emissions–Measurement Techniques and Fundamental Considerations. In *The Measurement and Control of Diesel Particulate Emissions;* Progress in Technology, Number 17; Society of Automotive Engineers: Warrendale, PA, 1979; pp 1-58.
422. Kittelson, D.B.; Dolan, D.F. Diesel Exhaust Aerosols. In *Generation of Aerosols and Facilities for Exposure Experiments;* Willeke, K., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 337-359.
423. Kittelson, D.B.; Watts, F.W., Jr.; Arnold, M. *Review of Diesel Particulate Matter Sampling Methods: Supplemental Report #2, Aerosol Dynamics, Laboratory, and On-Road Studies*; University of Minnesota, Department of Mechanical Engineering: 1998.
424. Kittelson, D.B.; Arnold, M.; Watts, W.F. *Review of Diesel Particulate Matter Sampling Methods—Final Report*; University of Minnesota; Center for Diesel Research: 1998.
425. Vogt, R.; Scheer, V.; Maricq, M.M. Nanoparticle Artifacts: Comparison of Tailpipe Dilution Tunnel Measurements of Vehicle PM. Presented at International ETH-Workshop on Nanoparticle Measurement, Zurich, Switzerland; ETH Zurich Labortorium für Festkorperphysik: 1999.
426. Shi, J.P.; Harrison, R.M. Investigation of Ultrafine Particle Formation during Diesel Exhaust Dilution; *Environ. Sci. Technol.* **1999**, *33(21)*, 3730-3736.
427. Khalek, I.A. Nanoparticle Growth during Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment. Presented at International ETH-Workshop on Nanoparticle Measurement, Zurich, Switzerland; ETH Zurich Labortorium für Festkorperphysik: 1999.
428. Pagán, J. *Study of Particle Size Distributions Emitted by a Diesel Engine*; 1999-01-1141; Society of Automotive Engineers: Warrendale, PA, 1999.
429. Abdul-Khalek, I.; Kittelson, D.; Brear, F. *The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements*; 1999-01-1142; Society of Automotive Engineers: Warrendale, PA, 1999.
430. Chen, J.-P. Particle Nucleation by Recondensation in Combustion Exhausts; *Geophys. Res. Lett.* **1999**, *26(15)*, 2403-2406.
431. Harris, D.B.; King, F.G.J.; Brown, J.E. Development of On-Road Emission Factors for Heavy-Duty Diesel Vehicles Using a Continuous Sampling System. In *The Emissions Inventory: Programs and Progress;* Publication No. VIP-56; Air and Waste Management Association: Pittsburgh, PA, 2000; pp 290-308.
432. Brown, J.E.; Clayton, M.J.; Harris, D.B. Comparison of Particle Size Distribution of Heavy-Duty Diesel Exhaust Using a Dilution Tailpipe Sampler and an In-Plume Sampler On-Road Operation; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 1407-1416.
433. Maricq, M.M.; Chase, R.E.; Podsiadlik, D.H.; Vogt, R. *Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements*; 1999-01-1461; Society of Automotive Engineers: Warrendale, PA, 1999.
434. Saxena, P.; Cass, G. Designing Atmospheric Experiments to Enable Estimation of Source-Receptor Relationships for Fine Particles. In *Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter;* PM Measurements Research Workshop, Chapel Hill, North Carolina; Health Effects Institute: Cambridge, MA, 1998.
435. Schauer, J.J.; Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Source Apportionment of Airborne Particulate Matter Using Organic Compounds; *Atmos. Environ.* **1996**, *30*, 3837-3855.
436. Meuzelaar, H.; Arnold, N.; Jarman, W. Paso del Norte Air Research Program, Scoping Study, Interim Report; Southwest Center for Environmental Policy and Research. http://www.scerp.org/, accessed 1999.
437. Burtscher, H. Measurement and Characteristics of Combustion Aerosols with Special Consideration of Photoelectric Charging and Charging by Flame Ions; *J. Aerosol Sci.* **1992**, *23(6)*, 549-595.
438. Burtscher, H.; Siegmann, H.C. Monitoring PAH-Emissions from Combustion Processes by Photoelectric Charging; *Combust. Sci. Technol.* **1994**, *101*, 327-332.

439. Burtscher, H.; Schmidt-Orr, A.; Siegmann, H.C. Monitoring Particulate Emissions from Combustion by Photoemission; *J. Aerosol Sci*. **1988**, *18*, 125.
440. Palmer, G.R. Ambient Air Monitoring of Fine Particulate Matter at Hill Air Force Base, UT and the Influence of Mobile Sources. M.S. Thesis, University of Utah, Salt Lake City, UT, 1999.
441. Chow, J.C.; Watson, J.G.; Pritchett, L.C.; Pierson, W.R.; Frazier, C.A.; Purcell, R.G. The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation and Application in U.S. Air Quality Studies; *Atmos. Environ.* **1993**, *27A(8)*, 1185-1201.
442. Chow, J.C.; Watson, J.G.; Crow, D.; Lowenthal, D.H.; Merrifield, T. Comparison of IMPROVE and NIOSH Carbon Measurements; *Aerosol Sci. Technol.*, in press.
443. Funkenbusch, E.F.; Leddy, D.G.; Johnson, J.H. The Characterization of the Soluble Organic Fraction of Diesel Particulate Matter. In *Measurement and Control of Diesel Particulates;* Society of Automotive Engineers: Warrendale, PA, 1979; pp 123-143.
444. Fraser, M.P.; Cass, G.R.; Bernd, R.T.S. Gas-Phase and Particle Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel; *Environ. Sci. Technol.* **1998**, *32(14)*, 2051-2060.
445. Hildemann, L.M.; Mazurek, M.A.; Cass, G.R. Quantitative Characterization of Urban Sources of Organic Aerosol by High-Resolution Gas Chromatography; *Environ. Sci. Technol.* **1991**, *25(7)*, 1311-1325.
446. Arnott, W.P.; Moosmüller, H.; Rogers, C.F.; Jin, T.; Bruch, R. Photoacoustic Spectrometer for Measuring Light Absorption by Aerosol: Instrument Description; *Atmos. Environ.* **1999**, *33*, 2845-2852.
447. Moosmüller, H.; Arnott, W.P.; Rogers, C.F.; Chow, J.C.; Frazier, C.A.; Sherman, L.E.; Dietrich, D.L. Photoacoustic and Filter Measurements Related to Aerosol Light Absorption during the Northern Front Range Air Quality Study (Colorado 1996/1997); *J. Geophys. Res.* **1998**, *103(D21)*, 28,149-28,157.
448. Arnott, W.P.; Rogers, C.F.; Sagebiel, J.; Zielinski, B.; Fujita, E.; Lighty, J.S.; Sarofim, A.F.; Griffin, J.B. Evaluation of Five Instruments for the Real-Time Measurement of Diesel Particulate Emissions. In *10th CRC On-Road Vehicle Emissions Workshop, San Diego, CA*; Coordinating Research Council, Inc.: Atlanta, GA, 2000.
449. Hopke, P.; Casuccio, G.S. Scanning Electron Microscopy. In *Receptor Modeling for Air Quality Management;* Hopke, P.K., Ed.; Elsevier: New York, 1991; pp 149-208.
450. Spurny, K.R. Review of Applications. In *Physical and Chemical Characterization of Individual Airborne Particles*; Spurny, K.R., Ed.; Ellis Horwood Series in Analytical Chemistry; Wiley: New York, 1986.
451. Kim, D.S.; Hopke, P.K.; Casuccio, G.S.; Lee, R.J.; Miller, S.E.; Sverdrup, G.M.; Garber, R.W. Comparison of Particles Taken from the ESP and Plume of a Coal-Fired Power Plant with Background Aerosol Particles; *Atmos. Environ.* **1989**, *23(1)*, 81-84.
452. Watt, J. Automated Characterization of Individual Carbonaceous Fly Ash Particles by Computer-Controlled Scanning Electron Microscopy: Analytical Methods and Critical Review of Alternative Techniques; *Water, Air, Soil Pollut.* **1998**, *106*, 309-327.
453. Webber, J.S.; Dutkiewicz, V.A.; Husien, L. Identification of Submicrometer Coal Fly Ash in a High-Sulfate Episode at Whiteface Mountain, New York; *Atmos. Environ.* **1985**, *19*, 285-292.
454. Eatough, D.J.; Eatough, M.; Lamb, J.D.; Lewis, L.J.; Lewis, E.A.; Eatough, N.L.; Missen, R. Apportionment of Sulfur Oxides at Canyonlands during the Winter of 1990—I. Study Design and Particulate Chemical Composition; *Atmos. Environ.* **1996**, *2*, 269-281.
455. Anderson, J.R.; Buseck, P.R. 5.3 Special Examples of Applications of Minerology and Geochemistry to Environmental Problems. In *Advanced Minerology*; Marfunin, A.S., Ed.; Springer-Verlag: Berlin, 1998; Vol. 3; pp 300-313.
456. Buseck, P.R.; Anderson, J.R. Analysis of Individual Airborne Mineral Particles. In *Advanced Minerology*; Marfunin, A.S., Ed.; Springer-Verlag: Berlin, 1998; Vol. 3; pp 292-299.
457. Suess, D.T.; Prather, K.A. Mass Spectroscopy of Aerosols; *Chem. Rev.* **1999**, *99*, 3007-3095.
458. Hughes, L.S.; Allen, J.O.; Kleeman, M.J.; Johnson, R.J.; Cass, G.R.; Gross, D.S.; Gard, E.E.; Gälli, M.E.; Morrical, B.D.; Ferguson, D.P.; Dienes, T.; Noble, C.A.; Liu, D.-Y.; Silva, P.J.; Prather, K.A. Size and Composition Distribution of Atmospheric Particles in Southern California; *Environ. Sci. Technol.* **1999**, *33(20)*, 3506-3515.
459. Reilly, P.T.; Gieray, R.A.; Whitten, W.B.; Ramsey, J.M. Real-Time Characterization of the Organic Composition and Size of Individual Diesel Engine Smoke Particles; *Environ. Sci. Technol.* **1998**, *32*, 2672-2679.
460. Gard, E.; Mayer, J.E.; Morrical, B.D.; Dienes, T.; Fergenson, D.P.; Prather, K.A. *Anal. Chem.* **1997**, *69*, 4083-4091.
461. Allen, J.O.; Fergenson, D.P.; Gard, E.E.; Hughes, L.S.; Morrical, B.D.; Kleeman, M.J.; Gross, D.S.; Gälli, M.E.; Prather, K.A.; Cass, G.R. Particle Detection Efficiencies of Aerosol Time of Flight Mass Spectrometers under Ambient Sampling Conditions; *Environ. Sci. Technol.* **2000**, *34(1)*, 211-217.
462. Serita, F.; Kyono, H.; Seki, Y. Pulmonary Clearance and Lesions in Rats after a Single Inhalation Dose of Ultrafine Metallic Nickel at Dose Levels Comparable to the Threshold Limit Value; *Ind. Health* **1999**, *37(4)*, 353-363.
463. Snow, J. *On the Mode of Communication of Cholera*. Reprinted in Snow on Cholera: A Reprint of Two Papers, 1965; Hafner Publ. Co.: New York, 1855.
464. Gertsman, B.B. *Epidemiology Kept Simple: An Introduction to Modern and Classical Epidemiology*; Wiley-LISS: New York, 1998.

EX 5

Supplier	Filter	Mass/area (oz./yd.)	Outlet PM2.5 Concentration (gr/dscf)
Hamon Research -Cottrell, Inc.	SunCoke proposed bag (PPS)	18	n/a, guarantee 0.005 PM
BWF America, Inc's	Grade 700 MPS Polyester Felt	18	0.0000086
Donaldson Company, Inc.	Tetratec #6255 Filtration Media	22	0.0000090
Donaldson Company, Inc.	6277 Filtration Media	8	0.0000034
Donaldson Company, Inc.	6282 Filtration Media	10	0.0000020
Southern Filter Media, LLC	PE-16/M-SPES Filter	16	0.0000220
W.L. Gore & Associates, Inc.	L3650 Filter	22	0.0000070
Air Purator Corp.	Huyglas 1405M Filter	22	0.0000065
Albany International Corp.	Primatex Plus I Filter	16	0.000014
BASF Corp.	AX/BA-14/9-SAXP Filter	14	0.00011
GE BHA Group, Inc.	QG061 Filter		0.0000009
GE BHA Group, Inc.	QP131 Filter		0.000003
BWF America, Inc.	Grade 700 MPS Polyester Felt Filter	18-20	0.0000045
Inspec Fibres	5512BRF Filter	16	0.00016
Menardi-Criswell	50-504 Filter	16	0.0000083
Polymer Group, Inc.	DURAPEX PET Filter	10	0.0000185
Standard Filter Corp.	PE16ZU Filter		0.0000041
Tetratec PTFE Technologies	Tetratex 6212 Filter	16	0.0000023
Tetratec PTFE Technologies	Tetratex 8005	16	0.000022
W.L. Gore & Associates, Inc.	L4347 Filter		0.0000059
W.L. Gore & Associates, Inc.	L4427 Filter		0.0000021

Test Procedure

Conditioning period with 10,000 rapid pulse cleaning cycles

Recovery period with 30 normal filtration cycles

Six-hour performance test period

Inlet particle concentration = 18.4 ± 3.6 g/dscm with average particle size of 1.5 micron diameter
= 8.0 ± 1.6 gr/dscf

**GE acquired and is still selling the BHA Group filters

Description	Status
	never verified
micro-pore-size, high-efficiency, scrim-supported felt, singed cake side	currently verified
woven fiberglass with Tetratex PTFE membrane	currently verified
Polyester Spunbond with Tetratex PTFE membrane	currently verified
Pleatable polyphenylene sulfide (PPS) with Tetratex PTFE membrane	currently verified
singed Micro-Denier polyester felt	currently verified
membrane/fiberglass fabric laminate	currently verified
PTFE film applied to a glass felt	prev. verified
polyethylene terephthalate filtration fabric with fine fibrous surface layer	prev. verified
	prev. verified
woven-glass-base fabric with an expanded, micro porous PTFE membrane	prev. verified
polyester needle felt substrate with an expanded, micro porous PTFE membrane	prev. verified
micro-pore size high efficiency scrim supported felt, singed cake side	prev. verified
100% scrim supported P84 needle felt	prev. verified
singed microdenier polyester felt	prev. verified
100 percent polyester, non-woven fabric, non-scrim supported	prev. verified
stratified microdenier polyester non-woven	prev. verified
polyester needle felt with Tetratex® expanded PTFE membrane	prev. verified
polyester scrim-supported needle felt with a Tetratex® expanded PTFE membrane	prev. verified
GORE-TEX® ePTFE (expanded polytetrafluoroethylene) membrane/polyester felt laminate	prev. verified
GORE-TEX® membrane/polyester felt laminate	prev. verified

	Outlet PM2.5 concentration (gr/dscf)		
	Best	Worst	Average
Currently verified	0.000002	0.000022	0.0000087
All verified (including expired)	0.0000009	0.00016	0.0000207

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April 18, 2008

VIA EMAIL AND HAND DELIVERY

Ms. Tamera Thompson
Virginia Department of Environmental Quality
629 E. Main Street
Richmond, Virginia 23219

Re: Comments on the Draft MACT Permit for the Virginia City Hybrid Energy Center

Dear Ms. Thompson:

The Southern Environmental Law Center, on behalf of itself, Appalachian Voices, Chesapeake Climate Action Network, Sierra Club, Southern Appalachian Mountain Stewards, Natural Resources Defense Council, and the National Parks Conservation Association respectfully submits the attached comments on the draft Maximum Available Control Technology (MACT) Permit for the Proposed Virginia City Hybrid Energy Center.

A hard copy of these comments, along with one binder containing 40 exhibits are being filed *via* hand delivery to the Department of Environmental Quality, at the DEQ headquarters in Richmond. Please date-stamp the additional copy for our records, to be returned with the courier.

In addition to the hard copy being filed in Richmond, we are also providing DEQ and members of the State Air Pollution Control Board with an electronic copy of these comments (without the exhibits and supporting documentation) via email. If you have any questions regarding this filing, or any other related matter, please do not hesitate to contact one of us at 434-977-4090.

Sincerely,

Sarah Rispin
Cale Jaffe

cc: Members of the State Air Pollution Control Board

TABLE OF CONTENTS

Comments on the Draft MACT Permit for the Virginia City Hybrid Energy Center
Exhibit List

Filed on behalf of Southern Environmental Law Center, Appalachian Voices, Chesapeake Climate Action Network, Sierra Club, Southern Appalachian Mountain Stewards, Natural Resources Defense Council, and the National Parks Conservation Association

1. E-mail from Golden to Thompson (Feb. 29, 2008). Subject: 38.6

2. Hendryx study, American Journal of Public Health (April 2008)

3. M. Cohen, NOAA, Modeling the Fate and Transport of Atmospheric Mercury in the Chesapeake Bay Region (May 17, 2004)

4. Landis *et al., Preliminary Results from Steubenville Hg Deposition Source Apportionment Study* (April 27, 2005)

5. Keeler, *et al.*, "Sources of Mercury Wet Deposition in Eastern Ohio, USA," *Environ. Sci. & Tech.* Vol.40, No. 19, at 5874 (2006)

6. Southern Environmental Law Center, Map of Mercury Pollution and Virginia's Children

7. Southern Environmental Law Center, Map of Mercury, Race and Poverty

8. Letter from Karen L. Mayne, U.S. Fish and Wildlife Service, to Kim Lanterman, Dominion Resources Services, Inc., Re: Proposed Dominion Power Plant, Wise County Virginia, USFWS # 51411-2008-TA-2005, (Dec. 1, 2007)

9. Letter from Karen L. Mayne, U.S. Fish and Wildlife Service, to Col. Dionysios Annios, U.S. Army Corps of Engineers, Re: Virginia City Hybrid Energy Center, Project No. 2007-03509, Wise County Virginia, (Dec. 11, 2007)

10. Foster Wheeler Spreadsheet of CFB Sample References

11. E-mail from Bazyk to Feagins (Feb. 25, 2008). Subject: Mercury Control Systems

12. Reliant Energy Seward Power Plant Summary of 2006 TRI Releases

13. Commonwealth of Kentucky Draft Air Quality Permit for Hugh L. Spurlock Generating Station (July 31, 2006)

14. E-mail from Zehner to Gregory (Feb. 15, 2008). Subject: Mercury BACT info

15. Power Point Presentation, "Mercury Emissions and Available Control Technologies for Combustion Sources" from the Department of Environmental Quality's Mercury and Clean Coal Technologies Work Group

16. E-mail from Zehner to Thompson (Feb. 25, 2008). Subject: Emissions Spreadsheet

17. E-mail from Spears to Buonviri (Feb. 26, 2008). Subject: mine locations

18. E-mail from McLeod to Thompson, Buonviri & Key (Feb. 26, 2008). Subject: USGS coal quality data

19. E-mail from Key to Buonviri (Feb. 28, 2008). Subject: Hg Number

20. E-mail from Key to Gregory (Feb. 29, 2008). Subject: Hg Number

21. E-mail from Dowd to Golden (March 4, 2008). Subject: HOLD – Proposed MACT Permit

22. E-mail from Zehner to Buonviri (Feb. 28, 2008). Subject: Powdered Activated Carbon Injected System Equipment

23. Draft Case-by-Case MACT Permit for VCHEC

24. Dominion Application for Case-by-case MACT Determination

25. E-mail from McLeod to Key (Feb. 28, 2008). Subject: Dominion MACT submittal

26. E-mail from Key toThompson (Feb. 28, 2008). Subject: non-mercury metals

27. USGS *Mercury in U.S. Coal – Abundance, Distribution and Modes of Occurrence* (Sept. 2001)

28. Toole-O'Neil *et al.,* "Mercury concentration in coal – unraveling the puzzle," *Fuel.* Vol. 78 (1999)

29. E-mail from Finto to Dowd (March 2, 2008). Subject: draft language

30. E-mail from Dowd to Buonviri (March 2, 2008). Subject: provisions for draft Wise Co. MACT permit

31. Draft PSD Permit for VCHEC

32. E-mail from Golden to Buonviri & Gregory (Feb. 20, 2008). Subject: blank

33. Engineering Analysis for Case-by-Case MACT Permit for VCHEC

34. R. Dwight Atkinson, Ph.D., EPA, "Virginia, REMSAD Mercury Deposition – 1998"

35. E-mail from McLeod to Buonviri (March 17, 2008). Subject: Other interesting stuff

36. E-mail from McLeod to Thompson (Feb. 28, 2008). Subject: DMME info from Abingdon

37. E-mail from Buonviri to Feagins & Thompson (Feb. 27, 2008). Subject: Fate of A6 and A8 permit

38. E-mail from Golden to Paylor (March 4, 2008). Subject: Hg MACT

39. E-mail from Buckheit to Paylor (March 4, 2008). Subject: Wise Co. MACT proposal

40. Miller, *et al.*, U.S. Department of Energy, National Energy Technology Laboratory, "Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants" (August 2006).

41. National Park Service, Total Mercury Wet Deposition 2005

42. National Park Service, Mercury Wet Deposition at Monitored National Parks

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April 18, 2008

VIA EMAIL AND HAND DELIVERY

Ms. Tamera Thompson, Air Permitting
Members of the State Air Pollution Control Board
Virginia Department of Environmental Quality
629 E. Main Street
Richmond, Virginia 23219

Re: Comments of Southern Environmental Law Center, Appalachian Voices, Chesapeake Climate Action Network, National Parks Conservation Association, Natural Resources Defense Council, Sierra Club, and Southern Appalachian Mountain Stewards, Regarding the Draft Case-by-Case MACT Permit for the Proposed Virginia City Hybrid Energy Center

Dear Ms Thompson and Members of the State Air Pollution Control Board:

The Southern Environmental Law Center (SELC), on behalf of itself, Appalachian Voices, Chesapeake Climate Action Network, National Parks Conservation Association, Natural Resources Defense Council, Sierra Club, and Southern Appalachian Mountain Stewards, respectfully submits the following comments on the draft case-by-case Maximum Achievable Control Technology (MACT) Permit for Virginia Electric and Power Company (Dominion), Registration No. 11526, to construct and operate an electric power generating facility at Alternate Route 58, Virginia City, Wise County, Virginia, noticed for public comment the Virginia Department of Environmental Quality (DEQ) on March 4, 2008.

I. INTRODUCTION.

On March 4, 2008, the Virginia Department of Environmental Quality (DEQ) issued to Virginia Electric and Power Company (Dominion) the first draft pre-construction permit required by the hazardous air pollutants (HAPs) provisions of the Clean Air Act, CAA § 112, for an electric utility generating unit (EGU) in the United States since the U.S. Court of Appeals' closely watched decision in *New Jersey v. EPA*[1]. In that decision, the Court of Appeals affirmed that the HAPs provisions do, in fact, apply to all EGUs in the country, including coal-fired power plants like Dominion's planned "Virginia City Hybrid Energy Center" (VCHEC), meaning that Dominion was therefore required to obtain a case-by-case Maximum Achievable Control Technology (MACT) permit prior to commencing construction.

Unfortunately, the process through which Dominion and DEQ produced this draft permit was woefully deficient. Dominion submitted to DEQ a cursory, five and a half page application on February 15, 2008—one week to the day after the D.C. Circuit issued its opinion in *New Jersey v. EPA*. DEQ issued the draft HAPs permit first thing in the morning on March 4, just ten business days later. As DEQ's Deputy Director, James Golden, said in an encouraging email to his staff on February 29, the last business day before the draft permit was published:

> Permit and EA [Engineering Analysis] look great *given the time we had to work on it* ... I think by Tuesday's publishing we will have a product better than I saw by any of the other states *and they did not do it in a week.*[2]

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[1] *New Jersey v. EPA,* No. 05-1097, slip op. (D.C. Cir. Feb. 8, 2008)
[2] Exhibit 1, Email from James Golden, DEQ, to Tamera Thompson, DEQ, "Subject: 38.6" (Feb. 29, 2008) (emphasis added).

One week, however, was simply not enough time to complete review of Dominion's thin and severely inadquate application. DEQ staff are hard-working, enthusiastic, and committed to environmental protection. Sadly, they were not given the opportunity to do their jobs. The draft permit and engineering analysis were simply rushed to completion. And the staff knew what the result in terms of quality was: While looking for support for their short-term emissions limit for mercury (which was based on the PSD permit's assumptions about the mercury content of coal, but not the MACT permit's assumptions)[3], staff members came across EPA's justification for that same short-term limit, which had been used in the now-vacated CAMR rule:

> A: "Here is how they justified 1.4 X 10)-5), which was published in the 6/9/06 [CAMR] FR and had very little explanation in it, in the response to comments ..."
>
> B: No worse than how we got our number. :-)

Exhibit 35, Mcleod-Buonviri email (Mar. 17, 2008). All this shows that the permit suffered because the emphasis appears to have been on meeting Dominion's timeframe for a quick turnaround rather than on meeting the minimum standards of the Clean Air Act's MACT requirements.

Accordingly, the permit and supporting documentation fail to consider, as required by the Clean Air Act, more than a small fraction of similar power plants to model controls for emissions of HAPs. The permit chooses the MACT emissions limit for HAPs from an irrelevant source, and ultimately HAPs emissions levels that are 10 to 50 times those of recently built similar plants. The Engineering Analysis fails to demonstrate, with the detail required by existing law and regulation, how the proposed VCHEC would comply with those limits. The draft permit and EA omit an entire section

[3] *See* further discussion of this at Section V.C, *infra*.

of the required analysis that should have inquired into whether it would be feasible for VCHEC to achieve emissions reductions more advanced than those of the similar power plants. The facility envisioned in the draft permit would not be required to take even the most basic steps toward further limiting emissions of HAPs: using alternative fuels, using high-rank, low-pollutant coal, washing or processing the coal it would use, using more efficient combustion technologies, or using well engineered systems marrying good combustion practices with innovative end-of-pipe control technologies to achieve the best possible HAPs emissions control levels. Finally, the permit includes a "safety valve," drafted by attorneys for Dominion, that makes it entirely optional for Dominion to comply with the fatally weak limits in the permit, at any rate.

The Clean Air Act's HAPs program is meant to push new industrial sources of these highly dangerous chemicals to use the most intelligent and advanced methods possible to limit their emissions. Congress and EPA established this program because of the extremely toxic effects of mercury and other HAPs on human health and the environment. The draft permit, however, fails to meet these standards. Rather, it would simply allow Dominion to emit *exactly the levels of toxics the company intended to emit all along,* before the D.C. Circuit's ruling in *New Jersey v. EPA* clarified that the company would have to comply with the HAPs provisions.

II. THE LIMITS IMPOSED BY THE DRAFT PERMIT ARE ILLUSORY.

Not only is the draft MACT permit fatally flawed, it is also, in fact, nonbinding by design. On this ground alone, it is violative of the Clean Air Act.

The Prevention of Significant Deterioration (PSD) draft permit published in January 2008 would require Dominion to remain below a mercury emissions rate of 71.93 lb/yr.[4] At first glance, the draft case-by-case MACT permit appears to lower that standard to 49.46 lb/yr.[5] However, on closer inspection, it is clear that the draft MACT limit is totally illusory.[6] The permit states in Condition 13:

> The annual mercury emission limit is based on an average of 0.3511 ppmw of mercury in the coal, a higher heating value of 6600 Btu/lb of coal and a 98% control efficiency. *Deviations from this limit* [of 49.46 lb/yr] *are allowed* if ... the permittee can document ... that the mercury content in the coal averages higher than 0.3511 pppmw and/or the higher heating value of the coal is less than 6600 Btu/lb.[7]

In other words, the draft MACT permit allows Dominion to exceed its mercury limits if it elects to use lower-quality coal than initially forecasted. The only real limit, then, is that imposed by the PSD permit.

Even more egregious is Condition 33 of the draft MACT permit, which allows for "optimization"[8] of the mercury number (that is, upward revision of the limit) *after* the permit has been finalized. If the applicant claims that the 49.46 lb/yr standard is not achievable, Condition 33 would allow even more unlawful exceedances of the mercury limit. Internally, DEQ refers to this provision as the "safety valve"[9] or "the out clause"[10]

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[4] *See* Exhibit 36, VCHEC, Draft PSD Permit, at 9. As a gauge, this is higher even than the mercury emissions of Mirant's Potomac River Generating Station in Alexandria, a conventional coal-burning power plant that first came online in 1949 and remains a notorious high-priority violator of Clean Air Act standards. *See* EPA, Toxic Release Inventory (TRI) data for 2003 for Mirant, Potomac River Generating Station (recording mercury emissions of 70.6 lb/yr).

[5] *See* Exhibit 23, VCHEC, Draft Case-by-Case MACT Permit, at 6.

[6] Additionally, as discussed in Section V.d., *infra*, while the annual limit is set at 49.46 lbs of mercury per year, the short-term limit is till the same 72 lbs/year that was in the PSD permit.

[7] *See id.* at 7, Footnote e (emphasis added).

[8] *See* Exhibit 29, Email from Kevin Finto, Hunton & Williams, to Michael Dowd, DEQ, "Subject: draft language," (March 2, 2008).

[9] *See* Exhibit 30, Email from Michael Dowd, DEQ to Patricia Buonviri, DEQ, "Subject: provisions for draft Wise Co. MACT permit," (March 3, 2008) .

[10] See Exhibit 21, Email from Michael Dowd, DEQ, to James Golden, DEQ, "Subject: FW: HOLD – Proposed MACT Permit," (March 4, 2008), which states:

because it would literally allow Dominion "out" of the company's permit obligations. It would allow the Wise County coal plant to violate the very mercury standard agreed to in the permit.[11]

> The "out clause" states:
>
> > [I]f the permittee reasonably demonstrates ... that the lb/MWhr and/or the lb/yr limit are not achievable on a consistent basis under reasonably foreseeable conditions, then testing and evaluation shall be conducted to determine an appropriate adjusted maximum achievable annual emission limit...[12]

DEQ explains that this language "provides some flexibility in the event the technology proves incapable of achieving the limit."[13] However, as explained elsewhere in these comments, the technology is well-proven to significantly reduce mercury emissions far below the permitted level in the draft MACT analysis.

More to the point, having such an "out clause" in the permit is a plain violation of the Clean Air Act. Precedent from the U.S. Court of Appeals for the D.C. Circuit makes it abundantly clear that DEQ and the Air Board cannot allow such exceedances, particularly when (as in this case) other similarly situated sources have *actually achieved* far lower emissions than those specified in the draft permit.[14]

> Since the short term limit was based on the highest sampled, worse case Va. Coal it is unclear why they can't achieve an instantaneous basis, much less a monthly basis. Also, I told them two days ago that they may want the out clause to address the short term limit as well, but they didn't appear concerned about it, they didn't propose it, and I wasn't going to expand the scope of the provision if they didn't request it.

[11] Exhibit 30, Email from Michael Dowd, DEQ to Patricia Buonviri, DEQ, "Subject: provisions for draft Wise Co. MACT permit" (March 3, 2008).
[12] *See* Exhibit 23, VCHEC, Draft Case-by-Case MACT Permit, at 19.
[13] Exhibit 32, Email from James Golden, DEQ, to Patricia Buonviri, DEQ, (Feb. 20, 2008).
[14] As the D.C. Circuit has recognized, "section [112(d)(3)] provides that 'the maximum degree of reduction in emission that is deemed achievable . . . shall not be less stringent than' what the best-performing sources 'achieve.' Section 112(d)(3) therefore limits the scope of the word 'achievable' in section [112(d)(2)]." *Cement Kiln*, 255 F.3d at 861. *See also Sierra Club v. EPA*, 479 F.3d 875 (D.C. Cir. 2007).

Even more telling is the fact that there is no scientific basis for Condition 33 whatsoever. It was not drafted by the scientific experts at DEQ, nor was it even drafted by the engineers at Dominion. Rather, the language was drafted by attorneys at Hunton & Williams LLP and submitted directly to DEQ for inclusion in the permit in an email (two days before publication of the draft permit).[15] The Hunton & Williams email further suggests that the "out clause" was not even subject to scientific review by Dominion engineers before being sent to DEQ. The email states:

> Following up on our call late on Friday here is some revised draft optimization language for the mercury limit. In order to expedite review of this language I am sending it to you [DEQ] and Dominion at the same time and must reserve the right to make changes.[16]

This was forwarded to DEQ staff responsible for the drafting of the permit with few edits, to be included "wherever you deem appropriate."[17]

Needless to say, a permit limit that can be upwardly adjusted after the fact is no limit at all. Rather, it is license to emit with impunity as much mercury as the company deems reasonable – presumably up to the 71.93 lb/yr standard in the draft PSD permit.[18] A firm limit for mercury emissions is required by law. Accordingly, it is clear that the

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[15] *See* Exhibit 29, Email from Kevin Finto, Hunton & Williams, to Michael Dowd, DEQ, "Subject: draft language," (March 2, 2008).

[16] *Id.*

[17] See Exhibit 30, Dowd-Buonviri email of March 03, 2008 ("Patty: Please insert the attached 'safety valve' language into the draft permit wherever you deem appropriate. If you have any questions, please call me on my cell phone . . . ").

[18] In fact, by Dominion's own calculation, the lb/MWhr standard in the permit of 0.000014 "is equivalent to 72 lbs/yr" as stated in the PSD permit. *See* Email from Robert M. Bisha, Dominion, to Michael Dowd, DEQ, "Subject: HOLD – Proposed MACT Permit," (March 4, 2008) . Surprisingly, Dominion asserts that "compliance [with the 0.00014 lb/MWhr standard] would be demonstrated on a monthly basis – This is not achievable." *Id.* This alone is strong evidence that Dominion already predicts violating its lax 49.46 lb/yr limit and will almost certainly seek an increase in the permitted amount pursuant to Condition 33.

"out clauses" in Condition 13, Condition, 33, and elsewhere[19] in the draft permit must be rescinded.

III. INSUFFICIENT CONTROLS OF MERCURY AND OTHER HAZARDOUS AIR POLLUTANT AT VCHEC WILL THREATEN PUBLIC HEALTH, THE ENVIRONMENT, AND THE ECONOMY.

The Clean Air Act lists mercury as a Hazardous Air Pollutant (HAP), or air toxic, due to the serious threat it poses to human health and the environment.[20] As a result of this designation, airborne emissions of mercury from sources such as coal-fired power plants are subject to the strictest Clean Air Act controls – the maximum achievable control technology, or MACT, requirements as explained in CAA § 112. In December 2000, EPA added facilities like VCHEC to the list of HAP source categories subject to the MACT requirements because "electric utility steam generating units are the largest domestic source of mercury emissions, and mercury in the environment presents significant hazards to public health and the environment."[21] Furthermore, "the implementation of other requirements under the CAA *will not adequately address* the serious public health and environmental hazards arising from such emissions."[22]

EPA based its conclusions on an extensive body of evidence: a 1998 statutorily mandated Report to Congress on "Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units" in which EPA evaluated the mercury emissions from

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[19] Similarly, the MACT for hydrogen fluoride is proposed as 0.00047 lb/MMBtu, with the caveat that a higher "secondary" limit of 0.0023 lb/MMBtu may be appropriate based on stack tests. Draft Permit at 6. In effect, the 0.00047 lb/MMBtu is meaningless.

[20] Clean Air Act § 112(b)(1), 42 U.S.C. § 7412(b)(1).

[21] 65 Fed. Reg. at 79825, 79830. Clean Air Act section 112(n)(1)(A) requires EPA to conduct a study of the public health hazards resulting from emissions of HAPs from electric utility steam generating units and to regulate these units under section 112 "if the Administrator finds such regulation is appropriate and necessary after considering the results of the study[.]" 42 U.S.C. § 7412(n)(1)(A).

[22] *Id* (emphasis added).

1,149 units at 464 coal-fired power plants; a National Academy of Sciences evaluation of "the available data related to the health impacts of methylmercury," and emissions data acquired by the United States Department of Energy, the regulated industry, and EPA itself.[23] EPA determined that "certain segments of the U.S. population (i.e., the developing fetus, subsistence fish-eating populations) are believed to be at potential risk of adverse health effects due to mercury exposures resulting from consumption of contaminated fish."[24] Based on this evidence, EPA concluded that "mercury is the HAP of greatest concern."[25] Furthermore, it was "entering U.S. water bodies and contaminating fish [a]s the result of air emissions."[26] Specifically, it noted, "electric utility steam generating units are the largest domestic source of mercury emissions."[27]

It is universally accepted that mercury exposure severely damages the human nervous system and kidneys and threatens the brain development of children. Nationally, between 316,588 and 637,233 children are estimated to be born each year having mercury levels associated with loss of IQ.[28] The loss of intelligence causes diminished productivity that lasts a lifetime. $1.3 billion is in lost productivity is specifically attributable to mercury emissions from domestic power plants.[29] In addition to lowering IQ, mercury causes other permanent neurological and developmental injuries that drain

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[23] 65 Fed. Reg. at 79827.
[24] *Id.* at 79830.
[25] *Id.* at 79827.
[26] *Id.* at 79827.
[27] Although EPA abruptly reversed its prior determination in 2005, on February 8, 2008, the U.S. Court of Appeals for the D.C. Circuit struck down as unlawful EPA's reversal of its December 2000 finding. Thus, the prior determination remains in effect and mercury emissions from newly proposed coal plants, such as Dominion's Wise County facility, must meet the Clean Air Act's most stringent MACT standards.

[28] Trasande, Landrigan, and Schechter, *Public Health and Economic Consequences of Methyl Mercury Toxicity to the Developing Brain*, Environmental Health Perspectives (May 2005).
[29] *Id.*

educational and public healthcare resources and diminish the quality of life for affected children and their families.[30]

As EPA has recognized, mercury is "highly toxic, persistent, and bioaccumulates in food chains."[31] Once industrial sources, including power plants, emit *airborne* elemental mercury, a portion of it is deposited in surface waters. Toxic mercury in surface waters enters the food chain when it is converted to methylmercury by bacteria. Methylmercury then concentrates in the flesh of fish and other aquatic organisms, eventually threatening human health.[32]

In recent years, the Virginia Department of Health (VDH) has issued mercury-related fish consumption advisories for largemouth bass, sunfish, chain pickerel, and catfish, among other commercially and recreationally popular fish species.[33] These mercury advisories have been for waters that, until recently, had been regarded as "remote" and among "Virginia's most pristine."[34] They include the Pamunkey River, the Mattaponi River, Dragon Run Swamp, the Piankatank River, the Great Dismal Swamp, Lake Drummond, and the Blackwater River.[35]

Indeed, there is no safe level of mercury contamination. In 2005 in Washington, D.C., EPA and local public health officials mandated the closure of a high school for several days, all because of a small number of "'BB-sized' droplets of mercury" found in

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[30] These impacts come on top of all the other well known health impacts of coal mining on local populations. It has been long-established, for example, that residents of coal mining communities suffer from higher rates of cardiopulmonary disease, hypertension, diabetes, and lung and kidney diseases. Residents of the Coalfields also have a significantly higher likelihood (64% increase) of developing chronic pulmonary disease. Exhibit 2, Hendryx study, American Journal of Public Health (April 2008).

[31] 65 Fed. Reg. at 79827.

[32] As EPA explained in 2000, "[b]ecause the developing fetus is the most sensitive to the effects of methylmercury, the greatest concern is the consumption of mercury contaminated fish by women of childbearing age. *Id.*

[33] Virginia Department of Health, Fish Consumption Advisories and Restrictions in Effect for Virginia Waterways, *available at* http://www.vdh.state.va.us/HHControl/fishingadvisories.asp.

[34] Springston, *supra.*

[35] Virginia Department of Health, Fish Consumption Advisories, *supra* note 16.

the school's basement.[36] That same year the Williamsburg Virginia City Council Chambers were closed, evacuated, and decontaminated—including replacing furniture and carpeting—when a small mercury spill was discovered.[37]

In addition to the public health and environmental problems, mercury pollution also poses a significant threat to Virginia's economy and culture. Fishing is a key industry in Virginia, and over time it has become a strong cultural tradition for many in this region. Commercial fishing remains a significant contributor to the state's economy. In 2004, Virginia's commercial watermen landed nearly 85 million pounds of seafood, valued at more than $170 million.[38] In 2003, recreational fishing supported more than 10,000 Virginia jobs, led to $604,142,622 in retail sales, $262,542,074 in salaries and wages, and $11,562,195 in state tax collections.[39] Mercury contamination in fish and seafood threatens the livelihood of independent and commercial fishermen and has the potential to negatively impact Virginia's economy.

Moreover, many in Virginia have historically made their livings or spent their recreational time on the state's waters. Mercury contamination of fisheries threatens this way of life. As then-Secretary of Natural Resources W. Tayloe Murphy, Jr. commented, "When I am at home in the Northern Neck it deeply saddens me to ride by one abandoned oyster shucking house after another – by lifeless crab picking facilities that

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[36] *See* Henri E. Cauvin & Donna St. George, "More Mercury Found at Cardozo," *The Washington Post*, (Mar. 7, 2005), at B1.

[37] *See* Editorial, "Time to Insist: Ask the candidates: Will You Cut Mercury Emissions?," *Newport News Daily Press*, (Sept. 29, 2005). The *Daily Press* opined, "Don't buy into a 'pass the buck' answer, that Virginia doesn't need to act because new rules on mercury emissions ... will address the problem. Those EPA regulations are so feeble they will protect the power companies but not huge numbers of American children. ... They are so pathetic a piece of environmental rulemaking that they faced a bipartisan effort in the Senate to repeal them just two weeks ago."

[38] Virginia Marine Resources Commission, Virginia Landings Bulletin, Commercial Fisheries Statistics, Annual Report 2004 (preliminary).

[39] American Sportfishing Association, Economic Impact of Sportfishing, 2003 State Overview, *available at* http://www.asafishing.org/asa/statistics/economic_impact/state_allfish_2003.html.

today stand empty – all monuments to a once thriving commercial seafood industry that no longer exists because we placed on that industry the cost of our failure to keep its workplace clean and healthy."[40] The failure to adequately address the state's mercury pollution problem could force many more Virginians to abandon traditions deeply rooted in their family and cultural identities.

DEQ and Air Board must also take into consideration the negative impact that mercury pollution from the proposed facility would have on the environmental health of the Great Smoky Mountains National Park (located 142-KM from the proposed site) and surrounding wilderness areas. Shenandoah National Park in Virginia and the Five United States Department of Agriculture Forest Service (USDAFS) managed lands are located within 250-KM of the proposed facility including; James River Face (in Virginia), Linville Gorge (North Carolina), Shining Rock (North Carolina), Cohutta (Georgia), and Joyce Kilmer-Slickrock (North Carolina).

Recent research in the eastern United States shows significant bioaccumulation of methylmercury in salamanders, Peregrine falcons and forest songbirds. In recent decades, the number of wood thrushes in the southeast region has declined 45 percent, and researchers now suspect that accumulation of mercury in forest ecosystems could be part of the cause. Many of these species are found in the Smokies, and are therefore likely to be similarly impacted.

The Great Smoky Mountains National Park already suffers from some of the highest levels of wet mercury deposition in the United States (See Figure 1 and Figure 2, attached as Exhibits 41 and 42). It is clear given the results of the 2006 "Sources of

[40] W. Tayloe Murphy, Jr., Remarks to the Environment Virginia Conference, Virginia Military Institute, Lexington, Va., (Apr. 11, 2005).

Mercury Wet Deposition in Eastern Ohio" EPA study that showed that wet mercury deposition clearly accumulates no more than 400 miles away and had been emitted no longer than three days earlier from a coal-fired power plant source.[41] If the Wise County facility is built as it is currently designed the Great Smoky Mountains and the many other natural areas in the region will be subject to mercury emitted from the VCHEC facility.

The scientific literature also tells us that any mercury emissions from the proposed Wise County VCHEC would deposit close to the plant, disproportionately impacting the poorest communities in Southwestern Virginia.

A substantial body of scientific evidence demonstrates that mercury emitted from power plants and other air emission sources deposits close to the source. EPA's own Regional Modeling System for Aerosols and Deposition (REMSAD) indicates that "[m]ost states have [mercury 'hot spot'] areas that are *significantly influenced* by sources within their boundaries."[42] In Virginia, for example, in-state sources are responsible for approximately half – 47% – of all mercury deposited at the state's most severe "hot spot."[43]

In addition, two studies conducted by the National Oceanic and Atmospheric Administration (NOAA) – one on the Great Lakes region and the other on the Chesapeake Bay – have determined that sources within sixty miles of a particular water body are responsible for the majority of mercury contamination in the water, despite the

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[41] Gerald J. Keeler, M.S. Landis, G.A. Norris, E.M. Christianson, and J.T. Dvonch, "Sources of Mercury Wet Deposition in Eastern Ohio, USA," Environmental Science and Technology (American Chemical Society), Vol. xx, No. xx, xxx (published online September 8, 2006).

[42] R. Dwight Atkinson, Ph.D., EPA, "Air Deposition Modeling and the TMDL Program: Mercury Loadings to States and Regions," *available at* http://www.northstar.sierraclub.org/campaigns/air/mercury/epaMercuryDepositionReport2003.pdf (Draft 2003) (emphasis added).

[43] *Id.*; "Virginia, REMSAD Mercury Deposition – 1998," (attached as Exhibit 34).

level of emissions from the distant sources.[44] Local emissions of mercury can account for 50% to 80% of mercury deposition in "hot spots."[45] The Chesapeake Bay study, for example, noted that sources more than 1550 miles (2500 kilometers) from the Bay emit more than five times as much toxic mercury as local sources within 62 miles (100 kilometers). Amazingly, despite this disparity, the local sources accounted for nearly thirty times as much of the mercury directly deposited in Bay waters.[46] The conclusion to be drawn from the data is clear – local sources significantly impact local mercury pollution problems.

The Great Lakes report, which resulted in a published, peer-reviewed article in the journal *Environmental Research*, concluded, "Overall, coal combustion in the United States was found to be the most significant source category contributing mercury through atmospheric deposition to the Great Lakes."[47] "For Lake Michigan," the NOAA researchers explained, "the contribution from the Chicago region stands out, due it is significant emissions *and proximity to the lake*.... For Lakes Erie and Ontario, contributions from the Ohio River Valley appear to be very significant, again, due to the high emissions in this region *and the comparative proximity to these lakes*."[48]

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[44] M. Cohen *et al.*, "Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes," 95 *Envt'l Res.* 247, 262-63 & fig. 14 (2004) (power plant contribution to Great Lakes mercury "hot spots"); Exhibit 3, M. Cohen, NOAA, Modeling the Fate and Transport of Atmospheric Mercury in the Chesapeake Bay Region (May 17, 2004) ("NOAA Chesapeake Bay") available online at http://www.arl.noaa.gov/data/web/reports/cohen/20_Ches_Bay_talk.pdf.

[45] *Id.*

[46] NOAA Chesapeake Bay, at 34 (graph showing "Emissions and Direct Deposition Contributions from Different Distance Ranges Away From the Chesapeake Bay").

[47] M. Cohen, *et al*, 95 Envt'l Res. 247, 262-63 (emphasis added).

[48] *Id.* at 261 (emphasis added).

These conclusions are further buttressed by studies of mercury deposition in Florida,[49] Wisconsin,[50] and Ohio.[51] It is inescapable that those communities closest to the mercury-emitting source (in this case, the Wise County area) will likely be the worst affected by the mercury contamination released. The health of the community depends on mercury pollution being controlled or eliminated to the greatest extent possible at the source.

In fact, an analysis of race and poverty in Virginia shows that the Commonwealth's poorest citizens and communities – like those in Wise County and Southwest Virginia generally – are disproportionately affected by mercury pollution. A map overlaying sources of mercury, contaminated waterways, and counties with high poverty rates shows that the Virginia's poorest citizens are most likely to be affected by mercury pollution.[52]

For example, the Blackwater River is bordered to the east and west by six of Virginia's ten largest industrial sources of mercury.[53] A recent mercury advisory on the

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[49] Florida Department of Environmental Protection, et al., *Integrating atmospheric Mercury Deposition with Aquatic Cycling in South Florida: An Approach for Conducting a Total Maximum Daily Load Analysis for an Atmospherically Derived Pollutant* at 57 (2003 ("[T]he dominant source term signal contributing to total mercury deposition in south Florida are local emissions."). The project was undertaken by the Florida Department of Environmental Protection, the United States EPA, the United States Geological Survey, The Florida Electric Power Coordinating Group, Florida State University, and the University of Florida, among others.

[50] T.R. Hrabik, C.J. Watras, "Recent Declines in Mercury Concentration in a Freshwater Fishery: Isolating the Effects of De-acidification and Decreased Atmospheric Mercury Deposition in Little Rock lake," *The Science of the Total Environment*, at 2, 8 (2002).

[51] Exhibit 4, Landis *et al., Preliminary Results from Steubenville Hg Deposition Source Apportionment Study* (April 27, 2005) ("Steubenville Study") . *See also* Exhibit 5, Keeler, *et al.,* "Sources of Mercury Wet Deposition in Eastern Ohio, USA," *Environ. Sci. & Tech.* Vol. 40, No. 19, at 5874 (2006) ("The dominant contributor to the mercury wet deposition was found … to be coal combustion (~70%). Meteorological analysis also indicated that a majority of the mercury deposition found at the Steubenville site was due to local and regional sources.").

[52] Exhibit 6, Southern Environmental Law Center, Map of Mercury Pollution and Virginia's Children ; Exhibit 7, Map of Mercury, Race, and Poverty .

[53] Lying just to the northwest of the river is the Chaparral Steel Plant, Cogentrix of Richmond, Chesterfield Power Station, and Stone Container Corporation-Hopewell. Lying just east of the river is the Yorktown

river impacts the City of Franklin, which is home to an International Paper plant that is a major source of airborne mercury pollution. Franklin also has 17.1% of its citizens living below the poverty line. More than one quarter – 26.4% – of Franklin's children aged seventeen and younger live in poverty. It is these children who bear the greatest brunt of Virginia's mercury contamination problem. And it is similarly situated families in Southwest Virginia who will be disproportionately affected by the unlawfully high mercury emissions from the proposed Wise County coal plant. Even more, as discussed elsewhere in these comments, Dominion's choice of low-Btu, high-mercury coal, such as unprocessed run-of-mine (ROM) coal, only exacerbates these adverse impacts.

Finally, because of the many threatened and endangered species living in and around the Clinch River, mercury emissions from the Wise County coal plant also threaten to violate the Endangered Species Act. The U.S. Department of the Interior, Fish and Wildlife Service (FWS) in a letter to Dominion on December 10, 2007, warned of Endangered Species Act concerns based on "air emission transport and deposition of heavy metals and other pollutants from the power plant."[54] The next day, in a letter to the Army Corps of Engineers, the FWS explained:

> Atmospheric deposition of pollutants from coal fired power plants occurs near and far-field of the point of emission. *We are concerned that emitted pollutants, such as mercury, may be taken by aquatic and terrestrial endangered species in the project vicinity...*. We recommend that the [Army] Corps [of Engineers] requires a biological assessment [under the Endangered Species Act] to evaluate the effects of atmospheric deposition of project air emissions.[55]

Power Station and the Chesapeake Energy Center. Collectively, these sources emit approximately 1,058 pound of mercury each year. *See* 2003 Toxic Release Inventory, Mercury Emissions in Virginia.

[54] Exhibit 8, Letter from Karen L. Mayne, U.S. Fish and Wildlife Service, to Kim Lanterman, Dominion Resources Services, Inc., Re: Proposed Dominion Power Plant, Wise County Virginia, USFWS # 51411-2008-TA-2005, (Dec. 1, 2007) .

[55] Exhibit 9, Letter from Karen L. Mayne, U.S. Fish and Wildlife Service, to Col. Dionysios Annios, U.S. Army Corps of Engineers, Re: Virginia City Hybrid Energy Center, Project No. 2007-03509,, Wise County Virginia, (Dec. 11, 2007) .

The FWS's comments about the potentially unlawful impact of high mercury emissions on federally endangered species further highlight the critical importance of reducing mercury emissions from the Wise County coal plant to the greatest extent possible.

Dominion's proposal to burn low-quality, unprocessed, unwashed, ROM coal in the Wise County facility will only worsen these adverse environmental and health impacts. The use of trucks to bring poor quality coal to the Dominion facility will add significant amounts of particulate matter (both PM-10 and PM-2.5) to the ambient air. Then, once this low-quality coal is burned, as much as 60 to 80% will be left behind as fly ash. Fugitive dust from the fly ash, of course, will contain significant amounts of heavy metals (such as mercury) that will impact the immediate air and water quality of Wise County. In other words, while burning unprocessed, ROM coal might be cheaper for Dominion, the health costs of that choice will undoubtedly be higher for the residents of St. Paul and Wise County.

IV. THE MAXIMUM ACHIEVABLE CONTROL TECHNOLOGY STANDARDS ARE THE STRICTEST CLEAN AIR ACT REQUIREMENTS IMPOSED BY CONGRESS.

In recognition of the heavy toll that mercury and other hazardous pollutants take on human health and the environment, Congress substantially tightened the Clean Air Act's provisions governing the emissions of hazardous air pollutants (HAPs) through the Clean Air Act Amendments of 1990. At that time, frustrated by EPA's slow pace in regulating HAPs, Congress:

> . . . added the list of pollutants to be regulated, regulation deadlines, and minimum stringency requirements to the Clean Air Act precisely because it believed EPA had

> failed to regulate enough HAPs under previous air toxics provisions. * * * "The legislation reported by the Committee would entirely restructure the existing law, so that toxics might be adequately regulated by the Federal Government."

National Lime Association v. EPA, 233 F.3d 625, 634 (D.C. Cir. 2000) (quoting S. REP. NO. 101-228, at 128 (1989)). The Clean Air Act lists more than 180 individual hazardous air pollutants that are subject to control by what it refers to as the "maximum available control technology," or MACT. CAA § 112 (b) (list of pollutants). A federal court ruling from February of this year makes it clear that power plants are now subject to this regime.

A. Coal-fired Power Plants, Such As The Proposed VCHEC, Are Subject To The Section 112 Requirements.

Coal-fired power plants have been subject to the CAA's HAPs regime since electric utility steam generating units ("EGUs"), of which coal-fired power plants are a subset, were first listed as a source category to which the HAPs regime applies in December 2000. *See* 65 Fed. Reg. 79,825 (Dec. 20, 2000). This listing was based on a decision by the EPA Administrator that it was "'appropriate and necessary' to regulate mercury emissions from coal- and oil-fired power plants under section 112." *New Jersey v. EPA,* 2008 U.S. App. LEXIS 2797 at *8 (D.C. Cir. Feb. 8, 2008). As EPA explained in the listing determination, "[c]oal- and oil-fired electric utility steam generating units are major sources (as defined in section 112(a)(1) of the CAA) of hydrogen chloride and hydrogen fluoride emissions . . . and are the leading anthropogenic sources of mercury emissions in the U.S." 65 Fed. Reg. at 79,828. In that listing determination, EPA further

noted that EGUs were major sources of arsenic, beryllium, cadmium, chromium, dioxins, formaldehyde, lead, manganese, and nickel. *Id.* at Table 1.

In 2005, however, the EPA issued a rule removing EGUs from the list of source categories subject to the CAA's HAPs provisions. This was reversed, restoring the status quo ante, on February 8th of this year, when the D.C. Circuit issued its opinion in *New Jersey v. EPA*. In that case, the D.C. Circuit made two critical rulings. First, it vacated the 2005 delisting rule. Second, it vacated the "Clean Air Mercury Rule" which was meant to replace HAPs for power plants.

The net effect of this ruling is that EGUs are once again listed under CAA § 112, and therefore subject to the HAPs provisions of the Act. The D.C. Circuit issued the mandate for this case on March 7, 2008, rendering this result binding law.

The HAPs provisions, which now apply to all coal-fired power plants, require that all new EGUs obtain a pre-construction permit. *See* CAA § 112(g)(2). This requires all new EGUs, including coal-fired power plants like VCHEC, to meet what is determined to be the "maximum available control technology" emissions level for their source.

MACT is a far stricter standard than the "best available control technology," or BACT, standards of the PSD program. At a minimum, the MACT standard "shall not be less stringent than the emission control that is achieved in practice by the best controlled similar source," CAA § 112(d)(3); 40 C.F.R. § 63.41, regardless of cost. *See National Lime Association v.* EPA, 233 F.3d 625, 640 (D.C. Cir. 2000) ("[C]ost may not influence the determination of a MACT floor, which depends exclusively upon the emission reductions achieved by the best-performing sources."). In other words, MACT is concerned not with what is *achievable* by the single source being permitted, but rather

with what is "*achieved in practice*" by a benchmark source in that source category, CAA § 112(d)(3), whether through end-of-the-pipe technological controls, or by other means, such as low-pollutant fuel. *See National Lime Association*, 233 F.3d at 634; *see also Cement Kiln Recycling Coalition v. EPA*, 255 F.3d 855, 861 (D.C. Cir. 2001). At a maximum, the MACT for a given source may be *more* strict than what has been achieved in practice by the best controlled similar source, if that increase in stringency is economically and technologically achievable for the source in question.

B. The HAPs Regime Requires A Thorough Case-by-case MACT Analysis for The Proposed VCHEC.

Because EPA has not yet determined a uniform MACT standard for all EGUs, a new plant such as VCHEC must undergo a case-by-case MACT analysis. *See* CAA § 112(g)(2)(B) ("Such determination shall be on a case-by-case basis where no applicable emission limitations have been established by the Administrator."); 40 C.F.R. § 63.40(c); Memorandum from John Seitz, U.S. EPA, to Regional Air Directors at 1 (Aug. 1, 2001).

The case-by-case MACT analysis has two primary steps: First, the authority must determine the emissions control level achieved by the "best controlled similar source" for each of the HAPs that the source will emit. That emissions control level, referred to as the "floor," establishes the minimum emissions limit, which the applicant must find a way to meet regardless of cost. Second, the applicant and permitting authority must look into whether it is possible to achieve a more stringent control level for each of those HAPs, at which point cost and other feasibility issues may be taken into consideration. This is called the "beyond the floor" standard. How to determine these two standards is explained more fully below.

1. At A Minimum, The Proposed VCHEC Must Meet The MACT "Floor."

The first step in this analysis is to ascertain the emissions control that is actually achieved by the best controlled similar source. *See* CAA § 112(d)(3); 40 C.F.R. § 63.43(d)(1) ("The MACT emission limitation or MACT requirements . . . shall not be less stringent than the emission control which is achieved in practice by the best controlled similar source ...."); *id.* at 63.41 (the MACT "emission limitation for new sources means the emission limitation which is not less stringent than the emission limitation achieved in practice by the best controlled similar source . . . ."). This is called a "floor," because the source being permitted cannot drop below this level of emissions control, regardless of the cost of achieving that level. *National Lime Association*, 233 F.3d at 629 (the emissions floor "appl[ies] without regard to either costs or the other factors and methods listed in [CAA] section [1]12(d)(2).").

To be clear, the actual level of performance of the best performing source *is* the MACT floor, even if the regulator can not identify how the source actually achieves its emissions control, or even if the best performing source does not intentionally control emissions at all. This is because to be recognized as the best performing similar source "requires neither an intentional action nor a deliberate strategy to reduce emissions." *Sierra Club v. EPA*, 479 F.3d at 882-83 (D.C. Cir. 2007). In short, with respect to MACT floors, method of control and universal achievability are categorically irrelevant;

if a proposed facility cannot achieve the MACT limit as configured, the facility must change its design.[56]

It follows from these principles that the MACT floor cannot be expressed as simply a percentage pollution reduction achieved by the benchmark source. Instead, it should be expressed as the lowest emission rate (in the case of EGUs, expressed as pounds per kWh mmBtu) that the benchmark achieves, whether through application of control technology, the use of less hazardous inputs, or another strategy.[57]

In other words, if the best controlled similar source reduces its emissions of mercury (or another HAP) by 98%, it is not enough that the source being permitted also reduce emissions by 98%. Instead, the analysis must determine the amount of mercury produced by the best controlled source *per* mmBtu or kWh, and limit the permittee to emitting that same amount *per* mmBtu or kWh. The best controlled similar source may not actually be reducing uncontrolled emissions at all, but may achieve those emissions levels unintentionally, *Sierra Club v. EPA*, 479 F.3d at 882-83, by using low-pollutant fuel, for instance. *Cf. Cement Kiln*, 255 F.3d at 863 ("The statute itself . . . directs EPA to consider factors such as 'process changes, substitution of materials or other modifications, . . . design, equipment, work practice, or other operational standards . . .

[56] As the D.C. Circuit has recognized, "section [112(d)(3)] provides that 'the maximum degree of reduction in emission that is deemed achievable . . . shall not be less stringent than' what the best-performing sources 'achieve.' Section 112(d)(3) therefore limits the scope of the word 'achievable' in section [112(d)(2)]." *Cement Kiln*, 255 F.3d at 861. *See also Sierra Club v. EPA*, 479 F.3d 875 (D.C. Cir. 2007).

[57] This interpretation is thought to be correct by members of the State Air Pollution Control Board *See* Exhibit 39, Buckheit-Paylor email ("[F]or new sources there is a new source 'floor' – no less stringent than the best performing similar unit & based on the Brick MACT decision [*Cement Kiln*] that is supposed to be the emission rate, not % removal.").

[or] a combination of the above, suggesting that 'Congress itself recognized that many factors . . . affect sources' emissions.).[58]

Conversely, a new facility that matches even an extremely high percentage reduction would not achieve that same emissions performance of the lowest emitting source if the fuel it planned on using had higher HAPs content than that used by the benchmark source. Allowing new plants to merely meet the percentage reduction, without regard to the ultimate emissions levels, would invite applicants to posit high HAPs-content fuel so that they could set high emissions limits as expressed in pounds or tons per year, laying out a roadmap for evasion.

2. DEQ Is Obligated To Determine What Is The "Best Controlled Similar Source."

This first step of the MACT analysis, of course, depends on what is defined as a "similar source" to the new source under consideration. The implementing regulations for CAA § 112 define a similar source as "a stationary source or process that has comparable emissions and is structurally similar in design and capacity to a constructed or reconstructed major source such that the source could be controlled using the same technology." 40 C.F.R. § 63.41.[59]

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[58] *See also* S. REP. NO. 101-228, at 168 ("The technologies, practices or strategies which are to be considered in setting emission standards under this sub-section go beyond the traditional end-of-the-stack treatment or abatement system. The Administrator is to give priority to technologies or strategies which reduce the amount of pollution generated through process changes or the substitution of materials less hazardous. Pollution prevention is to be the preferred strategy wherever possible.").

[59] EPA has ruled that similar sources for a plant such as VCHEC include coal-fired EGU equipped with a CFB boiler. *See In re: Indeck-Elwood, LLC*, 2006 EPA App. LEXIS 44, 142 (Sep. 27, 2006) (holding that a "similar source" to a proposed coal-fired power plant that was to use CFBs to burn petroleum coke, coal tailings, and some natural gas was "other CFBs.").

Thus, Dominion and DEQ should look to all coal-fired power plants that use CFB boilers. Further, they should consult the Control Technology Center as described in CAA section 113, the AIRS, including information in the MACT database. See 40 CFR 63.41.

3. Dominion Must Select A Technology That Meets the MACT "Floor."

Having identified the emissions control level achieved by the best-controlled similar source, the applicant must find a way to meet that standard, regardless of cost, *National Lime Association*, 233 F.3d at 629, and regardless of the need for major design changes. *See Sierra Club v. EPA*, 479 F.3d at 882-83 (D.C. Cir. 2007) (rejecting EPA's reliance on "a concern that floors based on clean [inputs] would be unachievable because of the inability of [sources] to switch [inputs]" as a reason for deviating from the MACT floor requirements of the CAA).

As already hinted at, it is not sufficient for the applicant to look just to end-of-the-pipe emissions controls. Instead, the applicant must look quite broadly for ways to control emissions, including all "measures, processes, methods, systems or techniques to limit the emission of hazardous air pollutants through process changes, substitution of materials, or other modifications." 40 CFR 63.40 (definition of "control technology."). *See also Cement Kiln*, 255 F.3d at 863 ("The statute itself . . . directs EPA to consider factors such as 'process changes, substitution of materials or other modifications, . . . design, equipment, work practice, or other operational standards . . . [or] a combination of the above, suggesting that 'Congress itself recognized that many factors . . . affect sources' emissions.); S. REP. NO. 101-228, at 168. ("The technologies, practices or strategies which are to be considered in setting emission standards under this sub-section

go beyond the traditional end-of-the-stack treatment or abatement system. The Administrator is to give priority to technologies or strategies which reduce the amount of pollution generated through process changes or the substitution of materials less hazardous. Pollution prevention is to be the preferred strategy wherever possible.").

Finally, the applicant must explain to the permitting authority how, exactly, it will comply with this "floor" level. Specifically, it must divulge "technical information on the design, operation, size [and] estimated control efficiency of the control technology." 40 C.F.R. § 63.43(e)(xi).

4. DEQ and Dominion Are Required To Look At Emissions Control Levels Beyond The "Floor" Standard.

Having found the floor, and explained how it will comply with that emissions control level, the applicant must further look at whether a still higher level of emissions control is "achievable" in light of "the cost of achieving such emission reduction, and any non-air quality health and environmental impacts and energy requirements." CAA 112(d)(2). *See also id.* at 112(d)(3) (the new source "shall achieve the maximum degree of reduction in emissions of HAPs which can be achieved by utilizing those control technologies that can be identified from the available information, taking into consideration the costs of achieving such emission reduction and any non-air quality health and environmental impacts and energy requirements associated with the emission reduction.").[60] This higher level of emissions control is referred to as the "beyond-the-floor" MACT. *See NRDC v. EPA,* 489 F.3d 1250, 1254 (D.C. Cir. 2007), *Cement Kiln*

[60] *See also* 40 C.F.R. 60.41 (MACT emission limitation is at minimum, the floor, but also "reflects the maximum degree of deduction in emissions that the permitting authority, taking into consideration the cost of achieving such emission reduction, and any non-air health and environmental impacts and energy requirements, determines is achievable ... .").

Recycling Coal. v. EPA, 255 F.3d 855, 857-58 (D.C. Cir. 2001) (per curiam) (explaining two-step MACT process for hazardous waste combustors); *National Lime Association v. EPA*, 233 F.3d 625, 628-29 (D.C. Cir. 2000) (same for portland cement manufacturing plants).

This is not a step that can be skipped. Every MACT standard must include a robust "beyond the floor" analysis to identify and evaluate all potential options for achieving greater emissions controls. Such analyses must be conducted for each HAP that a facility will emit, and must fully explore the possibility of reductions from emissions control technology as well as non-technology options (just as such an exploration must be included in the attempt to find a way to meet the MACT floor). *See* 40 CFR 63.40 (definition of "control technology"); *Cement Kiln*, 255 F.3d at 863; S. REP. NO. 101-228, at 168.

Only at this stage, as is evident from the language of CAA §§ 112(d)-(e), costs may be taken into limited consideration. MACT permit applicants must look at all available technologies and techniques for (further) reducing HAPs emissions, but only have to adopt those that are technically and economically feasible.

But the applicant cannot just dismiss more stringent controls out of hand: The applicant must provide evidence that it conducted this evaluation. According to EPA's implementing regulations, applicants must provide supporting documentation of the alternative control technologies that they considered and rejected in their "beyond the floor" analysis, including an explanation of the economic and non-air quality environmental costs of that technology. 40 CFR 63.43 (e) (xii). This analysis should include consideration of process changes, substitution of materials or other modifications,

clean fuels and fuel cleaning options, design, equipment, and work practice requirements, worker training, other operational standards, and any available combinations of these options.

When evaluating beyond the floor MACT standards, regulators must also specifically evaluate non-air quality environmental impacts. A failure to consider such impacts is impermissible. *National Lime Association*, 233 F.3d at 634 (remanding the beyond-the-floor determination because the agency "failed to consider non-air quality health and environmental impact of potential beyond the floor standards"). Further, the applicant must specify in detail how it will comply with this "beyond-the-floor" level, just as it must explain how it will comply with the "floor" level. *See* 40 C.F.R. § 63.43(e)(xi).

C. Virginia DEQ Is Obligated To Implement These MACT Requirements Under Its Delegated Authority to Implement the Clean Air Act.

As SELC mentioned in its comments on the draft PSD permit issued by the DEQ earlier this year, Virginia DEQ and the State Pollution Control Board share the responsibility of implementing the Clean Air Act on behalf of the federal government. Virginia's plan to implement the federal Clean Air Act (state implementation plan, or SIP) obligates the Virginia permitting authority to impose "enforceable emissions limitations and other control measures, means, or techniques . . . as may be necessary or appropriate to meet the applicable [CAA] requirements." CAA § 110(a)(2)(A), codified at 42 U.S.C. § 7410(a)(2)(A). In this instance, Virginia is required to implement the HAPs program, which means preventing the construction of any major source of hazardous air pollutants unless it "determines that the maximum achievable control

technology emission limitation under this section for new sources will be met." CAA § 112(g)(B).

Although Virginia has, through its SIP, accepted authority for implementing the HAPs program, the federal EPA retains authority to ensure the CAA is being faithfully implemented. See CAA § 167, codified at 42 U.S.C. § 7477 (instructing EPA to "take such measures, including issuance of an order, or seeking injunctive relief, as necessary to prevent the construction of a major emitting facility that does not conform to the requirements of this part . . . .").

D. Conflicts between Virginia State Law and the HAPs Provisions of the Clean Air Act Must Be Resolved In Favor of the Clean Air Act.

A final area of relevant law bears discussion at this point in the comments—how DEQ and the State Pollution Control Air Board should resolve any conflicts between Virginia state law and the federal Clean Air Act. Dominion has relied heavily on Va. Code § 56-585.1.A.6 in its decision not to consider fuel sources other than unprocessed, run-of-mine coal (and gob and wood waste) from southwestern Virginia, insisting that the Virginia statute obligates the Wise County coal plant to burn Virginia coal.[61]

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[61] Regardless of whether the use of local coal may be desirable from the prospective of promoting in-state economic development, the Virginia Code cannot be read as requiring solely Virginia coal, because doing so would be a blatant violation of the Commerce Clause of the federal Constitution, which "directly limits the power of the State to discriminate against interstate commerce." *Wyoming v. Oklahoma*, 502 U.S. 437, 454 (1992). Again, as explained in SELC's prior comments on the PSD permit for VCHEC, the United States' Supreme Court's ruling in *Wyoming v. Oklahoma* is particularly instructive, as it involved a challenge to an Oklahoma law requiring the use of in-state coal. The Court had little trouble in striking down the Oklahoma law as violative of the U.S. Constitution:

> [T]he Act expressly reserves a segment of the Oklahoma coal market for Oklahoma-mined coal, to the exclusion of coal mined in other States. Such a preference for coal from domestic sources cannot be characterized as anything other than protectionist and discriminatory, for the Act purports to exclude coal mined in other States based solely on its origin.

Assuming, *arguendo,* that this state law compels Dominion to burn the lowest quality, high-mercury content Virginia coal, it still would not authorize Dominion to avoid complying with the HAPs provisions of the Clean Air Act. Under the Supremacy Clause of the United States Constitution,[62] federal law will always pre-empt a state law "when the state law 'stands as an obstacle to the accomplishment and execution of the full purposes and objectives of Congress.'" *International Paper Co. v. Ouellette,* 479 U.S. 481, 491-92 (1987) (internal citations omitted) (finding that federal Clean Water Act pre-empts nuisance lawsuit premised on state law). *See also Geier v. American Honda Motor Co.,* 529 U.S. 861, 871-72 (2000) (application of state law "would take from those who would enforce a federal law the very ability to achieve the law's congressionally mandated objectives that the Constitution, through the operation of ordinary pre-emption principles, seeks to protect."). Thus, in this case, an overly zealous application of Va. Code § 56-585.1.A.6, or any state law requirement to "utilize Virginia coal," is pre-empted by the Clean Air Act, which requires DEQ and Dominion to complete a full and rigorous case-by-case MACT analysis.

The importance of considering fuel sources outside of Virginia is especially important in this case, given the high mercury content of Virginia coal. According to the U.S. Geological Survey (and as detailed in the chart below), coal mined in the central Appalachian area, including Virginia coal, has the second highest mean and median

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Wyoming, 502 U.S. at 455. "Indeed, when a state statute amounts to simple economic protectionism, a 'virtually per se rule of invalidity' has applied." Id.. at 454-55 (internal citations omitted).

[62] U.S. Const. art. VI, § 2, states: "This Constitution, and the Laws of the United States which shall be made in Pursuance thereof; and all Treaties made, or which shall be made, under the Authority of the United States, shall be the supreme Law of the Land; and the Judges in every State shall be bound thereby, any Thing in the Constitution or Laws of any State to the Contrary notwithstanding."

values for mercury in the country (after northern Appalachian). *See* USGS, *Mercury in U.S. Coal,* FS—095—01 (September 2001).

Coal-Producing region	Mercury (ppm)			Calorific Value (Btu/lb)		
	Median	Mean	No.	Median	Mean	No.
Appalachian, northern (PA, OH, WV)	0.19	0.24	1,613	12,570	12,440	1,506
Appalachian, central (WV, KY, VA, TN)	.10	.15	1,747	13,360	13,210	1,648
Appalachian, southern (TN, AL)	.18	.21	975	12,850	12,760	969
Eastern Interior (IL, IN, KY)	.07	.10	289	11,510	11,450	255
Fort Union (ND, SD, MT)	.08	.10	300	6,280	6,360	277
Green River (WY, CO)	.06	.09	388	9,940	9,560	264
Gulf Coast (GA, AL, FL, MS, LA, TX, AR, TN, KY, IL)	.13	.16	141	6,440	6,470	110
Pennsylvania Anthracite (PA)	.10	.10	51	12,860	12,520	39
Powder River (MT, WY)	.06	.08	612	8,050	8,090	489
Raton Mesa (CO, NM)	.05	.09	40	12,500	12,300	34
San Juan River (NM, CO, UT)	.04	.08	192	9,340	9,610	173
Uinta (UT, CO)	.04	.07	253	11,280	10,810	226
Western Interior (IA, MO, NE, KS, OK, AR)	.14	.18	286	11,320	11,420	261
Wind River (WY)	.08	.15	42	9,580	9,560	42

Median and mean values for mercury concentrations (in parts per million (ppm)) and calorific values (in British thermal unites per pound (Btu/lb)) on an as-received, whole coal basis for selected coal-producing regions in the United States

Source: USGS Fact Sheet FS—095—01 September 2001

Furthermore, there is no constraint in Va. Code § 56-585.1.A.6 or anywhere else in Virginia law that prevents Dominion from *processing* the run-of-mine coal it plans to use prior to combustion. It is simply illogical that Dominion would limit itself to using run-of-mine coal, when it could greatly improve the plant's environmental performance by treating the same fuel in a coal processing plant prior to burning it.

V. DOMINION'S MACT ANALYSIS IS THOROUGHLY AND IRREMEDIABLY FLAWED.

The case-by-case MACT analysis that Dominion submitted to the Virginia DEQ on February 15, 2008 as a rapid reaction to the D.C. Circuit's February 8th ruling in *New Jersey v. EPA* is exactly what one might expect of an application of that magnitude cobbled together in a week. What Dominion proposed is deficient—sometimes shockingly so—at every single step of the required analysis.

A. The "Floor" for Mercury Emissions Was Established Without Reference to All Similar Sources.

The first step in the case-by-case MACT analysis, as explained in Section IV, *supra*, is determining the "floor," or minimum, emissions rates for all the relevant HAPs, that are emitted by the best controlled similar source. Right off the bat, Dominion barely made a showing of conducting a real inquiry into what constitutes that benchmark source for the proposed VCHEC facility. It claims in its application that there is only one other "similar source" to which it can compare VCHEC for the purposes of finding the MACT emissions control level, namely Unit # 3 at the Spurlock plant in Kentucky. *See* Application at 4 ("The only similar source burning bituminous coal that we have identified as having been subject to the case-by-case MACT for mercury is Spurlock Unit 3.").

DEQ then states in its Engineering Analysis that "in determining MACT for the proposed units, DEQ . . . focused primarily on determinations for CFB boilers and boilers burning waste coal as similar units." Engineering Analysis at 5-6. DEQ cites to only five "similar" units: Spurlock (KY); NE Utilities (NH); Western Greenbrier Cogen (WV);

Thoroughbred Generating Co. (KY); and Mid-American Energy (IA). *See id.* at Appendix A.

This is curious because, as shown in the table below, there are multiple coal-fired power plants that use CFBs to burn waste coal in the U.S. to which Dominion and DEQ should have looked to determine the best controlled similar source. Records obtained from DEQ through a Virginia Freedom of Information Act ("FOIA") request show that DEQ obtained a spreadsheet of CFBs burning coal and coke that were built by the same manufacturer that has been engaged to design VCHEC—Foster Wheeler. *See* Exhibit 10, at 17. This spreadsheet showed that there are five Foster Wheeler CFB plants burning coal, coke, Texas lignite or gob with boilers of comparable capacity in the United States and nine more abroad. *Id.* None of these were included in DEQ's list of five "similar sources."

Indeed, DEQ had access to a list of *fifty* coal-fired power plants in the United States that had recently booked contracts for mercury control equipment—the vast majority using ACI. *See* Exhibit 11, Bazyk-Feagins email (Feb. 25, 2008) (forwarding spreadsheet of fifty coal-fired power plants that ordered the installation of mercury control equipment, that had been shared among Tamera Thompson, the Director of the Office of Air Permit Programs, and employee of the Southwest Regional office in July 2007). *Cf.* 40 C.F.R. § 63.41 (defining a similar source as "a stationary source or process that has comparable emissions and is structurally similar in design and capacity to a constructed or reconstructed major source *such that the source could be controlled using the same technology*.") (emphasis added). But still DEQ concluded, without analysis, that there were only five "similar" sources to the proposed VCHEC to which it should be

compared. This raises questions as to both the procedural and factual propriety of the application and engineering analysis.

Large CFB Waste Coal Facilities in the U.S.*

Plant	City	St	Capacity (MW)	Primary Fuel	Secondary Fuel	Year
Colver Power Project	Colver	PA	110	Gob	Propane	1995
Seward	Seward	PA	521	Gob		2004
Northampton Generating LP	Northampton	PA	108	Culm	Petroleum Coke	1995
E C Gaston		AL	254	Bituminous Coal	Gob	1960
Gorgas		AL	565	Bituminous Coal	Gob	1972
James H Miller Jr		AL	2,822.0	Bituminous Coal	Gob	1978
Victor J Daniel Jr		MS	1,000.0	Bituminous Coal	Gob	1977
Sunbury Generator	Shamokin Dam	PA	283.5	Bituminous Coal	Culm	1949
Cope		SC	417.3	Bituminous Coal	Gob	1996
Wateree		SC	771.8	Bituminous Coal	Gob	1970
Williams		SC	632.7	Bituminous Coal	Gob	1973
Chesterfield		VA	359.0	Bituminous Coal	Gob	1964
Clover		VA	848.0	Bituminous Coal	Gob	1995

* Waste coal facilities with generating capacity > 100MW.
Source: http://www.energyjustice.net/coal/wastecoal/facilities.html

1. The Procedure Used for Determining The Best Controlled Similar Source Was Deficient and Contrary to Law.

On the procedural end, because so many CFBs and waste coal facilities were excluded from either Dominion's or DEQs analysis, it is clear that the definition of

"similar source" used in the draft permit is at variance with that described in either 40 C.F.R. § 63.41, "a stationary source or process that has comparable emissions and is structurally similar in design and capacity to a constructed or reconstructed major source such that the source could be controlled using the same technology," or EPA case law. *See In re: Indeck-Elwood, LLC*, 2006 EPA App. LEXIS 44, 142 (Sep. 27, 2006) (holding that a "similar source" to a proposed coal-fired power plant that was to use CFBs to burn petroleum coke, coal tailings, and some natural gas was, simply, "other CFBs."). In fact, neither Dominion nor DEQ provides any information on the emissions levels of either the plants considered to be "similar sources," or the plants that were, with analysis, not considered "similar."

Further, Dominion clearly failed to consult "additional information" as required in the implementing regulations. There is no indication—either in the form of records included with the application or engineering analysis, or in the similar source Dominion found—that the company consulted the Control Technology Center, the AIRS, or information in the MACT database. *See* 40 CFR 63.41. Nor did Dominion check publicly available sources such as EPA's ICR database, which collects mercury emissions data pursuant to CAA § 112(n). A determination of a best controlled similar source without consultations of these databases (or, in DEQ's case, acknowledgment of sources that the Department may have had access to that identified better controlled sources) is arbitrary, capricious, and contrary to law.

2. Dominion's Process Failed to Identify The Best Controlled Similar Source.

Finally, as a factual matter, Spurlock Unit # 3 may not, in fact, be the best controlled similar source. There are plenty of other stellar candidates that neither Dominion nor DEQ considered. Perhaps the most glaring omission from this list is Reliant Energy's Seward facility in Pennsylvania, which is a 521-megawatt CFB facility burning only waste coal that came online in 2004. Seward emits just 1.04 pounds of mercury per year, according to EPA TRI data.[63] Because this is a similar source that achieves *far* smaller mercury emissions per unit of energy produced than would VCHEC at permitted levels, Dominion must either: (1) provide a legally cogent explanation of why this is not, in the company's eyes, a "similar source," or (2) actually commit to meeting this far higher benchmark.[64]

B. The MACT "Floor" Used Was Weaker Than The Achieved Emissions Of Dominion's Choice For "Best Controlled Similar Source."

Even assuming that Spurlock #3 was the best-controlled similar source, the MACT limit set in the draft permit does not actually demand compliance with Spurlock Unit 3's emissions rate. The per-unit emissions rate at Unit 3 is 2.65×10^{-6} lb/MMBtu. *See* Exhibit 13, Commonwealth of Kentucky Draft Air Quality Permit for Hugh L. Spurlock Generating Station (July 31, 2006) at 13, 19. But the draft permit for VCHEC does not use or prescribe this per-unit emissions rate. Instead, it uses a 98% mercury reduction effectiveness rate *that is unrelated to Spurlock.* This is problematic both

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[63] *See* Exhibit 12, Reliant Energy Seward Power Plant Summary of 2006 TRI Releases.

[64] Another similar source that is better controlled than VCHEC as permitted is the Brayton Point Station in Massachusetts, which burns bituminous coal and uses carbon injection, but has a mercury limit of 0.0075 lb/GWh. VCHEC's proposed limit of 0.000014 lb/MWh—expressed in the same terms as 0.014 lb/GWh—is 86% higher than the Brayton Point Station limit.

because the limit is not actually pegged to the source that Dominion claims is the best-controlled similar source, *and* because it is expressed as a percentage reduction.

According to correspondence between DEQ and Dominion on the day that Dominion submitted its application, DEQ apparently recommended the 98% removal efficiency rate to Dominion based on a Power Point presentation from the Mercury and Clean Coal Technologies Work Group for DEQ. *See* Exhibit 14, Zehner-Gregory email, (Feb. 15, 2008). The 98% figure comes from a four-item chart in that report that gives the percentage mercury removal achieved by four methods of mercury removal, with 98% being the highest of those four. *See* Exhibit 15 at 11. That 98% figure bears no relation to Spurlock Unit # 3—rather, it is (apparently) the percentage mercury removal achieved by the use of a spray dryer adsorber and fabric filter. *Id.* But just because 98% is the highest mercury reduction that happened to be noted in a non-comprehensive DEQ study done for other reasons does not mean that it is the highest possible reduction achieved.

Indeed, internal correspondence shows that Dominion and DEQ *knew* that 98% was lower than the real percentage reduction in mercury emissions at Spurlock Unit 3 which was, in fact, *99.6%*. In email correspondence, Dominion acknowledged that DEQ had already "determined that BACT [for mercury] was 99.6% based on Spurlock stack testing."[65] A Dominion representative went on to admit that "Dominion never submitted an application showing . . . 99.6% control" but rather that "98% control . . . is what Dominion proposed and included in the permit applications." *Id.* Apparently, when DEQ applied the more accurate 99.6% control number in an early draft of the permit, the

[65] Exhibit 16, Email from Jeffrey R. Zehner, Dominion, to Tamera Thompson, DEQ, "Subject: RE: Emissions Spreadsheet," (Feb. 25, 2008).

Department came up with a controlled mercury emission of 12 pounds per year, *id*, far less than the 49.46 pounds per year DEQ ultimately authorized in the published version of the draft permit.

In other words, Dominion and DEQ did not follow the process required by CAA § 112 in determining the floor *at all*. Not only is there no basis for saying that Spurlock Unit 3 is the best controlled similar source, but the figure Dominion included in its application and that DEQ accepted is lower than what Spurlock Unit 3 achieved.[66] The draft MACT permit should be rejected as contrary to law on this basis alone.

C. The MACT "Floor" Is Impermissibly Keyed To Percentage Reduction, Resulting In An Impermissibly High MACT Limit.

Although the HAPs provisions of the CAA require permittees to achieve the same emissions limit expressed in per-unit controls as the best-controlled similar source, *see* Section IV.B.1, *supra*, the draft permit would allow VCHEC to achieve this floor if it matched the same *percentage* reduction. This is clearly problematic, because reading the law as allowing MACT permits to designate a percentage reduction rather than a per-unit limit provides a roadmap to evasion. A permittee limited only by a percentage reduction could nonetheless emit dangerously high levels of toxic mercury by relying on the cheapest, lowest quality, highest-mercury content coal it could find.

In fact, this appears to be precisely what Dominion proposes to do, as demonstrated by ample record evidence. In the end, the draft permit states that the

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[66] SELC, *et al.*, are not stating that a 99.6% reduction would represent MACT in this case. First, as explained in subsection C, *infra*, MACT should not be expressed merely as a percentage reduction. Second, as we noted earlier, Dominion and DEQ have no basis for identifying Spurlock Unit 3 as the benchmark "best controlled similar source," since they did not cast their nets wide enough to have any basis for this choice. Rather, this discussion is meant to illustrate that Dominion would not even meet the benchmark it has established for itself – namely, the percentage reduction achieved at Spurlock #3.

"annual mercury emission limit is based on an average of 0.3511 ppmw of mercury in the coal." Draft Permit at Condition 13 (e). But Dominion pushed hard to have the annual mercury emission limit based on an assumed mercury value of 5.1 ppm of mercury.

DEQ rejected this, because 5.1 ppm represents the *highest* mercury content of coal that could be found in all of the mines Dominion told DEQ that it planned to use. *See* Exhibit 17, Buonviri-Spears email (Feb. 26, 2008) (DEQ employee disclosing chart of mercury content in coal from several mines in southwest Virginia to employee of the Virginia Department of Mines, Minerals and Energy). This is far dirtier than almost any coal being burned in the United States. As one DEQ Air Quality Planner described the 5.1 ppm figure after consulting the US Geological Survey's coal quality database, coal with 5.1 ppm of mercury "was at about the 98.9% (percentile) of the array so it appears to be a *darn high number.*" *See* Exhibit 18, McLeod-Thompson email of Feb. 26, 2008 (emphasis added).

Indeed, Patricia Buonviri, the Air Toxics Coordinator for DEQ, confirms in an email to Ms. Thompson that the 5.1 ppm assumption was not the average mercury figure for coal from the mines Dominion said it planned to use. *See* Exhibit 19, Key-Buonviri email (Feb. 28, 2008). Nor, she pointed out, was it even the average of the *worst* case mercury coal from *each* mine; those averages, reduced by 98%, would have produced emissions rates of 17.2 lb/yr or 38 .6 lb/yr, respectively. *Id.* Both of these were much lower than the emission limit of 72 lbs/year from the PSD permit that had been based on the 5.1 ppm assumption. It therefore had to be the worst case mercury coal from the single worst mine among those Dominion planned on using.

Ultimately, after a great deal of internal discussion and subsequent conversations with Dominion, DEQ chose to assume that the coal Dominion would use had a mercury content of 0.3511 ppmw based not on the requirements of the Clean Air Act, but rather out of an attempt to set an emissions output level that Dominion would willingly accept.

One official apparently sent out word that he was "looking for a [sic] high, medium and low number options, assuming the high would be status quo." *Id.* On the low end, Ms. Buonviri said that her "preference would be the 38.60 lb/yr (rather than the 49.46)" which was based on a number lower than 0.3511 ppmw, "because it uses the mines [Dominion] plans to use but still uses the worst case hg number for each mine." *Id.* Mike Gregory noted in an email to Margaret Key, a permit program auditor at DEQ, that the 38.6 lb/yr figure [based on a number lower than 0.3511 ppmw] would be "close to the upper end of EPA's [abandoned] 2004 MACT proposal." *See* Exhibit 20, Key-Gregory email (Feb. 29, 2008). But ultimately they settled at 0.3511 ppmw when Ms. Key replied that "I think for now we are going with a limit of 49.46 [lb]py on mercury. This is what [DEQ head] Dave Paylor agreed to tell Dominion that we are planning to put in the draft permit[, although] it is possible that we would go lower based on information provided during the public comment period." *Id.*

This analysis is an entirely impermissible way of determining an emissions control level, which is supposed to be pegged solely to the emissions limit achieved *in practice* by the best controlled similar source. Accordingly, the mercury emissions limit proposed in the draft MACT permit is arbitrary, capricious, and contrary to law.

D. DEQ Set The Short-Term Mercury Limit to Meet CAMR and PSD Requirements, Not MACT.

On the day the draft permit issued, worried that they had been given the 49.46 annual limit based on 0.3511 ppmw mercury coal, rather than the 72 pound annual limit from the PSD permit based on the 5.1 ppm mercury coal, Dominion still asked Michael Dowd, Director of the Air Quality Division at DEQ, to hold publication of the permit because the company was not satisfied with the short term limit on mercury emissions.

Meanwhile, however, DEQ had already accommodated Dominion on the short-term limit. They set the short-term limit at 1.4×10^{-6} lbs/MW-hr—the standard, in fact, that had been set in the Clean Air Mercury Rule vacated by *New Jersey v. EPA*, and a standard that translated to annual emissions of 72 pounds of mercury per year—so that Dominion could have more flexibility. *See* McLeod-Key Email of Feb. 28, 2008 ("I think this is good support for Patty's proposal to use the [CAMR] 1.4 x 10-6 lbs/MW-hr as the short term limit, to give the facility flexibility when burning the gob. Since they won't burn gob all the time, she has plenty of defense [agains Dominion criticisms] for cranking down on the long term annual limit, I think.").[67]

For this reason—in light of their generosity in considerably relaxing the short-term limit to match the CAMR standard—DEQ officials were surprised that Dominion still complained. Mr. Dowd, forwarding Dominion's request to another colleague at DEQ noted "[s]ince the short term limit was based on the highest sampled, worst case Va. Coal it is unclear why they can't achieve [it] on an instantaneous basis, much less a

[67] DEQ hid the fact that they were borrowing the standard from the vacated CAMR rules. *See, e.g.,* Exhibit 37 Buonviri-Feagins email (Feb. 27, 1008) ("Our concern is that if we reference Da in the Article 7 permit and EPA then pulls the mercury provisions out of Da, we could have a problem in the Article 7 permit. We just wanted to put in the direct wording in the A7 permit in case that were to happen, so no reopening would be required.").

monthly basis." *See* Exhibit 21, Dowd-Golden email (Mar. 4, 2008). *See also* Exhibit 38, Golden-Dowd email (Mar. 4, 2008) ("Dave, I find it curious that Dominion is surprised by the monthly short term limit in the MACT. . . . The MACT contains 0.000014 lb/MW-hour. . . . [I]t is still considerably more than 1/12 the annual number [of 49.46 lbs/yr].").

E. Dominion's Description of The Compliance Methodology Is Inadequate.

Even if the 98% reduction in mercury emissions were acceptable as the MACT floor, Dominion still fails to present an adequate analysis or description of how it will comply with this limit. In its application, Dominion describes the technology with which it plans to control HAPs as follows:

> To control SO2 and acid gas HAP emissions, limestone will be injected along with the coal into the CFB boiler. Dry flue gas desulfurization downstream of the boiler will provide additional control of SO2 and acid gas HAPs. The CFB boiler design itself will limit NOx formation and selective non-catalytic reduction (SNCR) will further reduce NOx emissions. Activated carbon injection (ACI) will be installed to enhance the removal of mercury and organic HAPs. The fabric filter will be employed to control the emissions of particulate and HAP metals.

Id. The only further elaboration provided by the company is as follows:

- "Mercury emissions will be controlled by . . . adsorption by activated carbon injected prior to the fabric filter . . ." Application at 3.
- "Furthermore, activated carbon will be injected into the flue gas upstream of the fabric filter. As a result, elemental and divalent forms of mercury may be reduced through adsorption onto the carbon . . . " *Id.* at 3-4.
- "[W]hen DEQ contemplated the potential of more stringent mercury standards . . . Dominion agreed to install activated carbon should the [BACT] limit not be met. Dominion now agrees to install activated carbon injection to meet the MACT emissions." *Id.* at 4.

- "The organic HAPs will be further controlled by the activated carbon injected into the flue gas upstream of the fabric filter baghouse." *Id.* at 5.

The Clean Air Act and implementing regulations require more than that an applicant just name a control technology. Rather, Dominion must provide sufficient information to satisfy the permitting authority that it will, in fact, achieve the emissions level of the best controlled similar source. *See* 40 C.F.R. § 63.43(e)(xi) (requiring application to include "technical information on the design, operation, size [and] estimated control efficiency of the control technology.").

During the review process, Tamera Thompson and Patricia Buonviri at DEQ asked Dominion for further information on the ACI system. In response, Jeff Zehner of Dominion explained only the following:

> The Powdered Activated Carbon (PAC) Injection system will include the following equipment:
>
> PAC Storage Silo
> PAC Feed System
> PAC Injection Grids
>
> Although *the system has not yet been designed*, it operates in the following fashion. Carbon is fluidized by air nozzles at the bottom of the silo. The carbon in the head space of the silo flows into the feeder/blower assembly which blows the PAC into the injection grids located in the flue gas ducts. The silo is filled via truck and a pneumatic transfer system. The fill frequency depends entirely on carbon usage.

Exhibit 22, Zehner-Buonviri email (Feb 28, 2008) (emphasis added). Clearly, Dominion's statements fail to satisfy the reporting requirements of 40 C.F.R. § 63.43(e). More shocking is Mr. Zehner's statement that "the system has not yet been designed"—two business days before the draft permit was released, no less. Without an actual design in place, there is no assurance that the system would actually achieve the proscribed

mercury emission limits. DEQ should have rejected the application for failure to comply with the reporting requirements, and failure to ensure that the MACT would actually be achieved.

F. The MACT "Floor" Proposed for Other HAPs Is Lacking in Basis and Is Under-Described.

In addition to the flaws detailed on mercury emissions, Dominion's determination of the MACT floor for all non-mercury HAPs is also seriously deficient. The application addresses three categories of HAPs besides mercury: (1) metals, including antimony, arsenic, beryllium, cadmium, chromium, cobalt, manganese, lead, nickel, and selenium; (2) acid gases, including hydrogen chloride and hydrogen fluoride; and (3) organic HAPs (not specified). *See* Application at Table 1. The applicant only briefly discusses how these HAPs will be controlled and groups materially different HAPs together, ignoring salient differences between various hazardous pollutants that VCHEC will emit.

Conveniently, Dominion concludes that the best available control technology (BACT) already prescribed in the draft PSD permit for all these pollutants *is also* the MACT. *See, e.g.,* Application at 4 ("Using the combination of a furnace limestone injection and dry flue gas desulfurization are as stringent as the controls currently used by the best similar source and therefore are considered MACT for hydrogen chloride and hydrogen fluoride."); *id.* at 5 ("Because the proposed controls [of a fabric filter baghouse, from the PSD permit] are as stringent as those applied to the best similar source, fabric filtration is considered MACT for other HAP metals.").

The draft permit then baldly asserts, without basis, that the BACT is MACT for non-mercury metals, and that the emissions control levels should be "99.9% . . . for

cobalt and lead; 99.8% for arsenic, beryllium, and manganese; 99.7% for antimony; 98.9% for nickel; 98% for chromium; 95.6% for cadmium; 90% for selenium." Exhibit 23, Draft Permit at 8 n 2. But it is very unlikely to be true that BACT constitutes MACT. BACT and MACT are very different standards, insofar as BACT takes economic factors into account, and the MACT floor determination cannot consider economic factors.

DEQ was aware that this was a problem. For example, the Dominion application provides the following explanation for why BACT is MACT for volatile organic HAPs:

> The proposed [PSD] control for volatile organic HAPs is as stringent as that applied to the emission controls achieved in practice by the best-controlled similar source and therefore is considered MACT.

Dominion Application, Exhibit 24 at 5, ¶4.4. One might expect an explanation as to why the BACT control levels in the PSD permit are "as stringent as that applied to the emission controls achieved in practice by the best-controlled similar source," but there is none. As Doris McLeod, an air quality planner at DEQ remarked in an email to Margaret Key, (after Ms. Key asked her to "read/re-read the Dominion application . . . to see if there is anything in the first 6 pages you really think cannot be supported?"):

> The information they provide in the second paragraph of 4.4 is pretty sketchy. If Patty [Buonviri] has found lower emissions rates for VOC that have been demonstrated, the second paragraph may border on a fib.

Exhibit 25, McLeod-Key email (Feb. 28, 2008). This exchange did not, however, result in any demand for additional information as to how Dominion determined that BACT was MACT for VOCs, nor any change in the standard.

Elsewhere, the draft permit fails to justify insupportable MACT levels submitted by Dominion. Dominion proposes that the MACT floor for hydrogen chloride (HCl) is

0.0066 lb/MMBtu, and that it can be achieved using the same limestone injection, a flash dryer absorber, and fabric filter prescribed in the PSD permit. But as the DEQ itself notes in its engineering analysis, lower limits have been demonstrated—Spurlock Unit 3 has a limit of 0.0035 lb/MMBtu.[68] But ignoring that even what they have chosen as the "best controlled similar source" achieves lower emissions limits than what Dominion proposes as MACT for HCl, DEQ argues that the higher (0.0066) limit is justified on the basis that "higher HCl emissions also enhance the removal of mercury..." Engineering Analysis at 10. Even if this were true, there is no analysis to demonstrate that mercury removal would be constrained if they limited HCl emissions to the levels achieved by Spurlock Unit 3. At any rate, the mercury emissions limit in the draft permit is itself quite lenient. Arguing for a lenient HCl limit to justify a lenient mercury limit makes little sense.

Additionally, the application concludes, with no discussion or rationale, that maximum controls of these HAPs will be achieved when the boiler is operating at its maximum rated operating capacity. But this is not necessarily the case. Many of the organic HAPs, for example, are likely created during periods of poor or incomplete combustion, making it more plausible that emissions of the organic HAPs will be higher when the boiler is operating at lower, less efficient, levels. Thus, there are no assurances that the emissions levels projected when the boiler is operating at maximum capacity will actually be the highest emissions levels seen.

Finally, even assuming the following unsupported string of assertions—that BACT is MACT for all non-mercury HAPs, that it is sufficient to express them in

[68] Even lower limits have been demonstrated. For example, Unit 3 at the Cross Generating Station in South Carolina, burning bituminous coal, has a HCl limit of 0.0024 lb/MMBtu.

percentage reductions rather than emissions levels, that the control levels will be achieved by the chosen technology operating at all capacities—the application, engineering analysis and draft permit provide no way to to assess whether the percentage reductions specified will, in fact, be met. This is because the application provides uncontrolled emissions levels for the non-mercury HAPs with no support whatsoever. The application states that the HAPs cited were "based on CFB design data, fuel composition, and emission factors cited in...AP-42," but AP-42 itself is vague, and the CFB design data and fuel composition for non-mercury HAPS are unspecified. Indeed, the DEQ staff could find no basis in Dominion's application for the uncontrolled emissions it put forward, concluding that the levels were probably back-engineered from the desired emissions limits by Dominion. *See* Exhibit 26, Key-Thompson email of Feb. 28, 2008 ("I talked with Mike. He says the numbers [for non-mercury HAPs] came from several different emission factor sources, some for wood and some for coal. Also he thought in at least some cases Dominion started with a controlled factor and back-calculated the uncontrolled number."). This makes it entirely impossible to test, going forward, whether the percentage reductions Dominion claims will be made in those HAPs will occur at all.

G. No "Beyond-the-Floor" Analysis Was Performed.

The application and draft permit have also failed to comply with what should be the next step in the MACT analysis after establishing the floor—looking into whether it would be feasible to achieve any further controls that go *beyond the floor*. Here—but not

only here[69]—Dominion and DEQ should have considered other methods and controls to reduce mercury emission further, but did not. In other words, it is not enough, under the HAPs regime, to determine the MACT *floor* and comply with that. Permittees must further look to see what other methods they can employ to achieve *further* reductions, and employ those that are feasible, to fully comply with the Act. Dominion entirely omitted this step.

1. Dominion Presents the VCHEC Project As Set in Stone.

As in its PSD permit, from the outset, Dominion presents certain aspects of the project as set in stone, and does not even consider changing them. Dominion signals its unwillingness to look at alternatives to its existing plan at the beginning of the application, where it explains the project as follows:

> The proposed project will consist of two identical coal-fired, circulating fluidized bed (CFB) boilers having a net nominal capacity of 585 megawatts (MW). The CFB boilers will be fired with Run-of-Mine bituminous coal and supplemental fuels, including waste coal and waste wood.

Exhibit 24, Dominion Application at 1. And indeed, Dominion does not consider the most basic and cost-effective options for mercury reduction beyond the floor—using alternate fuels, washing the coal, processing the coal, let alone using alternative combustion systems—*anywhere* in its MACT application.

[69] It is possible that Dominion would have needed to look into the whole range of alternatives that CAA § 112(g) would have them consider—all "measures, processes, methods, systems or techniques to limit the emission of hazardous air pollutants through process changes, substitution of materials, or other modifications," 40 CFR 63.40—in order to achieve the MACT *floor*. But there is no way of assessing whether they should have done so, since the application and draft permit utterly fail to establish what a legitimate floor should be, or whether the technology Dominion has chosen is capable of meeting that floor.

2. Dominion Should Have Considered A Wide Range Of Alternatives In Its "Beyond-the-Floor" Analysis.

The Clean Air Act's HAPs provisions are technology forcing. They are designed to compel applicants to use every tool at their disposal to (a) match the emissions levels achieved by the best controlled similar source, and (b) exceed that level of achievement where possible. As the implementing regulations for the HAPs provisions specify, a MACT applicant must look to all "measures, processes, methods, systems or techniques to limit the emission of hazardous air pollutants through process changes, substitution of materials, or other modifications." 40 CFR 63.40 (definition of "control technology.").

Dominion should have engaged in precisely this sort of search to determine if it could achieve reductions beyond the floor—beyond the level achieved by the "best controlled similar source." Because it engaged in no such analysis *at all*, there is not even a "beyond the floor" analysis to critique. There are, however, a long list of alternatives that DEQ was aware of that would have helped Dominion achieve further reductions. These include:

- **Switching from coal to natural gas**. DEQ officials reviewing Dominion's permit consulted a USGS document on mercury emitted from coal-fired power plants that suggested switching from coal to natural gas to limit mercury emissions. Exhibit 27, USGS, *Mercury in U.S. Coal—Abundance, Distribution and Modes of Occurrence* (Sept. 2001). But DEQ did not make this suggestion, nor did Dominion consider doing this.

- **Use of high-rank coals**. The same document explained that "[o]ne option to reduce the quantity of coal in the atmosphere [from coal-fired power plants] is to

use high-rank coals. Generally, moisture in coal decreases and calorific value (thermal energy) increases as coal rank (degree of maturation) increases. . . . [F]or coals having similar mercury concentrations, the higher rank coals will contribute less mercury to the environment." *Id.* But DEQ ignored this, and went along with Dominion's attempt to find the highest mercury-content coal possible so that it could get the highest limits possible.

- **Selective mining of coal**. The USGS document also suggests "avoiding parts of a coal bed that are higher in mercury content." *Id.* Nowhere in its analysis of Dominion's application did DEQ suggest that Dominion should have considered avoiding the coal with mercury levels of 5.1ppm that drove its unlawfully high mercury-emissions limit of 49.6 lbs/year, to reduce emissions from that level.

- **Coal washing**. Again, the same document recommended coal washing "to reduce the amount of mercury in the coal delivered to the powerplants." *Id.* A study cited in that report, conducted by the USGS in collaboration with industry, shows that, on average, 37% of the mercury is removed by coal cleaning. *See* Exhibit 28, Toole-O'Neil et al, 1999. DEQ also had a separate USGS document before it, Exhibit [number], USGS, *Mercury in Coal Website* (printed out 2/28/2008) with a highlighted section that explains that "Many Eastern U.S. bituminous coals are 'cleaned' prior to use in utility power stations, to reduce sulfur emissions. . . . In doing so, a portion of the mercury present may also be

removed, as a co-benefit of sulfur reduction." But again, nowhere did DEQ suggest to Dominion that it consider washing the coal.

- **Considering Integrated Gasification Combined Cycle (IGCC) as an alternate combustion method.** In the DEQ Mercury and Clean Coal Technology Work Group document from which the 98% mercury reduction figure was pulled, DEQ itself created a chart showing that whereas CFBs burning coal or coke would result in mercury emissions at the rate of 1.09 x 10-5 lbs per mmBtu, IGCC would result in mercury emissions at the rate of 1.94 x 10-6 lbs per mmBtu. *See* Exhibit 15 at 14. In simpler terms, this shows that CFB combustion produces more than 5.6 *times* the amount of mercury per mmBtu that IGCC does. But nowhere does DEQ ask Dominion to consider switching to IGCC, or examine the technical and economic feasibility of doing so.

- **Considering Supercritical Pulverized Coal.** In the same report, DEQ said that using supercritical pulverized coal technology would result in mercury emissions at the rate of 2.39 x 10-6 lbs per mmBtu. *See id.* This shows that CFB combustion produces more than 4.5 times the amount of mercury per mmBtu that super critical pulverized coal does. But nowhere does DEQ ask Dominion to consider switching to that technology, either.

- **Consideration of SCR Instead of SNCR To Improve Co-Benefit Reductions of Mercury.** It is well-established that Selective Catalytic Reduction systems to

reduce nitrogen oxide emissions can also help deliver significant co-benefits of mercury reduction when mated to FGD for sulfur control.[70]

- **Consideration of Alternative Mercury Reduction Technologies.** There may be other control technologies that should be considered. For example, Dominion consider ROFA™ and ROTAMIX™ controls, technology developed by Mobotec USA, which has shown impressive mercury reductions in full-scale evaluations.[71]

In sum, because Dominion's application and DEQ's engineering analysis entirely omit to conduct *any* beyond-the-floor analysis, the draft permit should be rejected as contrary to the HAPs provisions of the Clean Air Act. As a matter of policy, the importance of requiring Dominion and DEQ to fully explore all the options for further reducing mercury is made evident in the major reductions in mercury and other HAPs emissions that the list of possible changes above would allow.

VI. CONCLUSION.

SELC, *et al.,* recognize that harshness and severity of many of the criticisms outlined in these comments, and we do not make these criticisms lightly. As stated at the outset, we have the greatest respect for the individual staff at DEQ, who work diligently to meet their commitments to environmental protection. Yet in this case they simply were not provided with the opportunity to do their jobs. The entire MACT process –

[70] Miller, *et al,* U.S. Department of Energy, National Energy Technology Laboratory, "Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants" (Aug. 2006)(Exhibit 40).
[71] *See* Mobotec USA, Inc., Full-Scale Evaluation of a Multi-Pollutant Reduction Technology: SO2, Hg, and NOx, Paper #117, *available at* www.mobotecusa.com.

from initial application, to engineering analysis, to draft permit – was completed in less than one month. To meet Dominion's schedule for commencing construction, the draft permit and EA were cobbled together in one week. In contrast, the timeframe for completing the draft PSD permit was a year and a half, from July 2006 to January 2008.

Needless to say, this case-by-case MACT permit is woefully deficient. On mercury emissions alone, it would allow the proposed VCHEC to emit nearly *fifty times* as much mercury as Reliant Energy's 521-megawatt CFB plant in Seward, Pennsylvania. At 71.93 lb/yr PSD limit (which, because of the "out clause," may be the only firm limit applicable to the plant) VCHEC would emit more than *six times* as much mercury per-megawatt as Dominion's own Clover Power Station in Halifax County. Clover, which came online in 1996,also uses Wise County, Virginia coal.

But this is not a case merely of faulty numbers or impermissibly high emissions limits. The fundamental process by which the draft permit was completed is flawed and fails to comply with existing federal law and regulations. As a result, the draft case-by-case MACT permit must be rescinded.

Respectfully Submitted,

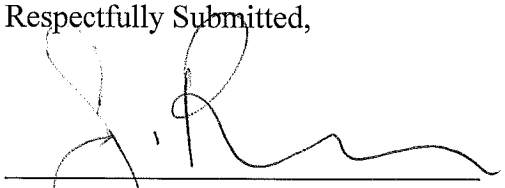

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Table A

#	HAP Name
1	ANTIMONY
2	ARSENIC
3	BARIUM
4	BERYLLIUM
5	CADMIUM
6	CHLORIDE
7	CHROMIUM
8	CHROMIUM(VI)
9	COBALT
10	COPPER
11	FLOURIDE
12	LEAD
13	MANGANESE
14	MERCURY
15	MOLYBDENUM
16	NICKEL
17	SELENIUM
18	VANADIUM
19	CHLOROMETHANE
20	BROMOETHANE
21	TRICHLOROFLUOROMETHANE
22	VINYL CHLORIDE
23	CHLOROETHANE
24	METHYLENE CHLORIDE
25	CARBON DISULFIDE
26	1,1-DICHLOROETHENE
27	1,2-DICHLOROETHANE
28	CHLOROFORM
29	1,2-DICHLOROETHANE
30	2-BUTANONE
31	1,1,1-TRICHLOROETHANE
32	CARBON TETRACHLORIDE
33	VINYL ACETATE
34	1,2-DICHLOROPROPANE
35	CIS-1,3-DICHLOROPROPYLENE
36	TRANS-1,3-DICHLOROPROPYLENE
37	TRICHLOROETHENE
38	1,1,2-TRICHLOROETHANE
39	BENZENE
40	BROMOFORM
41	4-METHYL-2-PENTANONE
42	TETRACHLOROETHENE
43	1,1,2,2-TETRACHLOROETHANE
44	TOLUENE
45	CHLOROBENZENE

46	ETHYL BENZENE
47	STYRENE
48	ACRYLONITRILE
49	ALLYL CHLORIDE
50	1,3-BUTADIENE
51	CUMENE
52	1,2-EPOXYBUTANE
53	ETHYL ACRYLATE
54	ETHYLENE DIBROMIDE
55	ETHYLIDENE DICHLORIDE
56	HEXANE
57	n-HEXANE
58	METHYL METHACRYLATE
59	METHYL TERT BUTYL ETHER
60	VINYL BROMIDE
61	O-XYLENE
62	M/P-XYLENE
63	XYLENES
64	METHYL ETHYL KETONE
65	METHYL BROMIDE
66	METHYL CHLOROFORM
67	3-CHLOROPROPYLENE
68	TRICHLOROMETHANE
69	1,2-DIBROMOMETHANE
70	4-ETHYL TOLUENE
71	1,3,5-TRIMETHYLBENZENE
72	1,2,4-TRIMETHYLBENZENE
73	1,3-DICHLOROBENZENE
74	BENZYL CHLORIDE
75	ACETOPHENONE
76	HEXACHLOROETHANE
77	NAPHTHALENE
78	HEXACHLOROBUTADIENE
79	2-CHLOROACETOPHENONE
80	HEXACHLOROCYCLOPENTADIENE
81	BIPHENYL
82	DIBENZOFURANS
83	2,4-DINITROTOLUENE
84	HEXACHLOROBENZENE
85	PENTACHLOROPHENOL
86	4-AMINOBIPHENYL
87	ANILINE
88	O-ANISIDINE
89	BENZIDINE
90	BIS-(2-ETHYLHEXYL)PHTHALATE
91	O-CRESOL(2-methylphenol)
92	M/P-CRESOL
93	P-CRESOL
94	CUMENE
95	1,2-DIBROMO-3-CHLOROPROPANE
96	DIBUTYLPHTHALATE
97	1,4-DICHLOROBENZENE
98	3,3-DICHLOROBENZIDENE

99	DICHLOROETHYL ETHER
100	N,N-DIMETHYLANILINE
101	3,3-DIMETHOXYBENZIDINE
102	DIMETHYL AMINOAZOBENZENE
103	3,3'-DIMETHYL BENZIDINE
104	DIMETHYL PHTHALATE
105	2,4-DINITROPHENOL
106	HYDROQUINONE
107	ISOPHORONE
108	4,4'-METHYLENEDIANILINE
109	NITROBENZENE
110	4-NITROBIPHENYL
111	4-NITROPHENOL
112	N-NITROSODIMETHYLAMINE
113	N-NITOSOMORPHOLINE
114	PENTACHLORONITROBENZENE
115	PHENOL
116	P-PHENYLENEDIAMINE
117	O-TOLUIDINE
118	1,2,4-TRICHLOROBENZENE
119	2,4,5-TRICHLOROPHENOL
120	2,4,6-TRICHLOROPHENOL
121	TRIFLURALIN
122	PHTHALIC ANHYDRIDE
123	2-METHYLNAPHTHALENE
124	1-METHYLNAPHTHALENE
125	2-CHLORONAPHTHALENE
126	ACENAPHTHYLENE
127	ACENAPHTHENE
128	FLUORENE
129	PHENANTHRENE
130	ANTHRACENE
131	FLUORANTHENE
132	PYRENE
133	BENZ(a)ANTHRACENE
134	CHRYSENE
135	BENZO(b)FLUORANTHENE
136	BENZO(k)FLUORANTHENE
137	BENZO(b+k)FLUORANTHENE
138	BENZO(e)PYRENE
139	BENZO(a)PYRENE
140	INDENO(1,2,3-c,d)PYRENE
141	DIBENZ[DE,KL]ANTHRACENE (perylene)
142	DIBENZO(a,h)ANTHRACENE
143	BENZO(g,h,i)PERYLENE
144	5-METHYL CHRYSENE
145	7H-DIBENZO(C,G)CARBAZOLE
146	DIBENZO(a,e)PYRENE
147	DIBENZO(a,h)PYRENE
148	DIBENZO(a,i)PYRENE
149	DIBENZ(a,h)ACRIDINE
150	DIBENZ(a,i)ACRIDINE
151	FORMALDEHYDE

152	ACETALDEHYDE
153	ACROLEIN
154	PROPIONALDEHYDE
155	CYANIDE
156	HYDROGEN CHLORIDE
157	HYDROGEN FLUORIDE
158	PHOSPHORUS
159	CHLORIDE PARTICULATE
160	FLUORIDE PARTICULATE
161	CHLORINE
162	FLUORINE
163	2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN
164	1,2,3,7,8-PENTACHLORODIBENZO-P-DIOXIN
165	1,2,3,4,7,8-HEXACHLORODIBENZO-P-DIOXIN
166	1,2,3,6,7,8-HEXACHLORODIBENZO-P-DIOXIN
167	1,2,3,7,8,9-HEXACHLORODIBENZO-P-DIOXIN
168	1,2,3,4,6,7,8-HEPTACHLORODIBENZO-P-DIOXIN
169	OCTACHLORODIBENZO-P-DIOXIN
170	2,3,7,8-TETRACHLORODIBENZOFURAN
171	1,2,3,7,8-PENTACHLORODIBENZOFURAN
172	2,3,4,7,8-PENTACHLORODIBENZOFURAN
173	1,2,3,4,7,8-HEXACHLORODIBENZOFURAN
174	1,2,3,6,7,8-HEXACHLORODIBENZOFURAN
175	1,2,3,7,8,9-HEXACHLORODIBENZOFURAN
176	2,3,4,6,7,8-HEXACHLORODIBENZOFURAN
177	1,2,3,4,6,7,8-HEPTACHLORODIBENZOFURAN
178	1,2,3,4,7,8,9-HEPTACHLORODIBENZOFURAN
179	OCTACHLORODIBENZOFURAN
180	TETRACHLORODIBENZO-P-DIOXIN
181	PENTACHLORODIBENZO-P-DIOXIN
182	HEXACHLORODIBENZO-P-DIOXIN
183	HEPTACHLORODIBENZO-P-DIOXIN
184	TETRACHLORODIBENZOFURAN
185	PENTACHLORODIBENZOFURAN
186	HEXACHLORODIBENZOFURAN
187	HEPTACHLORODIBENZOFURAN
188	K-40
189	Pb-210
190	Pb-211
191	Pb-212
192	Po-210
193	Ra-226
194	Ra-228
195	Th-228
196	Th-229
197	Th-230
198	Th-232
199	Th-234
200	U-234
201	U-235
202	U-238